

Formation and Rearrangement of Adducts from Benzyne and Substituted 2,1,3-Benzoselenadiazoles

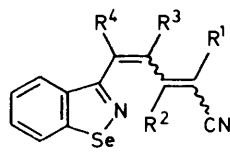
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A series of 5-(1,2-benzoselenazol-3-yl)pentadienonitrile derivatives (2) has been prepared by addition of benzyne to substituted 2,1,3-benzoselenadiazoles. Some of these adducts rearrange either thermally or photochemically to give 2-(2-pyridyl)phenyl selenocyanates (7), which are reduced to 2-phenylpyridine derivatives (6) or hydrolysed to give ultimately, diselenides (9). The crystal structure of one benzyne adduct (2b) is reported and the mechanism of its rearrangement discussed.

BENZYNE and 2,1,3-benzoselenadiazole (1a) give the 1 : 1 adduct (2a) by a remarkable rearrangement of the original heterocyclic system.¹ Proof of the structure (2a) rests upon detailed n.m.r. spectroscopic evidence, analogy to the isoxazole derivative (3a),² and ozonolysis to give 1,2-benzoselenazole-3-carbaldehyde. We now report the



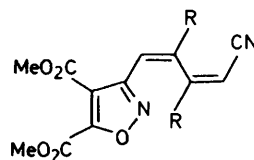
(1)



(2)

- a ; R¹ = R² = R³ = R⁴ = H
 b ; R¹ = R⁴ = H, R² = R³ = Me
 c ; R¹ = R³ = R⁴ = H, R² = Me
 d ; R¹ = R³ = R⁴ = H, R² = Cl
 e ; R¹ = R⁴ = Br, R² = R³ = H
 f ; R¹ = R⁴ = Br, R² = R³ = Me
 g ; R¹ = R⁴ = H, R² = R³ = Cl

a-i; substituents and stereochemistry as in Table 1



(3)

- a ; R = H
 b ; R = Me

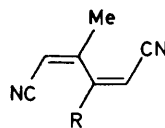
characterisation of the related benzyne adducts from a series of substituted 2,1,3-benzoselenadiazoles (1b–e) and the rearrangement of some of these adducts (2) into biaryl selenocyanates.

RESULTS AND DISCUSSION

The new 1,2-benzoselenazole derivatives (2b–i) are listed in Table 1 together with essential ¹H n.m.r. data. All of them were obtained in lower yield than the parent adduct (2a), and isomeric adducts were imperfectly separated from one another. All showed i.r. absorption close to 2 200 cm⁻¹ for a conjugated nitrile. All except (2e) showed the ¹H n.m.r. signal for one proton (R¹ = H_a) upfield of all the others due to shielding by the nitrile group. The splitting of this signal, J_{ab}, is crucial for the

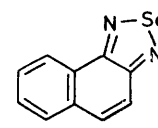
assignment of structure, showing whether the CN group is *cis* or *trans* with respect to the side-chain or, by the absence of splitting of this magnitude (>10 Hz), that the adjacent carbon is substituted (R² ≠ H). The same resonance also shows a weaker splitting where R¹ = R⁴ = H, except in the case of adduct (2b), in which the side-chain is very much out of plane (see below). The magnitude of this splitting is greater (J_{ad} ca. 1.6 Hz) for a *cis,cis* side-chain stereochemistry (*i.e.* with H_a and H_d *trans,trans*) than it is for a *cis,trans* configuration (J_{ad} ca. 0.6 Hz), in accord with observations made on other substituted butadienes.³ In the spectra of those adducts in which R² = H_b, another resonance could be identified as that of H_b, using double-resonance techniques to decouple the AB spin system.

Two of these adducts (2c and g) have a *trans* configuration of the nitrile-substituted double bond, although it is likely that addition of benzyne gives an all-*cis* configuration in the first instance.¹ With a substituent R² ≠ H it is more difficult to assign the stereochemistry from n.m.r. evidence. Adduct (2b) has the *cis,cis*-stereochemistry and both H_a and H_d give quartets in the n.m.r. spectrum; the splitting (J_{HMe} 1.6 Hz) is similar to those reported for compounds (4a and b), also having the *cis* configuration.^{4,5} However, the magnitude of the splitting cannot distinguish with certainty between geometrical isomers.⁶ An analogous adduct (2i) was obtained in low yield from benzyne and naphtho-[1,2-*c*][1,2,5]selenadiazole (5); its structure, which is established by the n.m.r. data (Table 1) and other



(4)

- a ; R = Me
 b ; R = H



(5)

evidence (see Experimental section), shows surprisingly that addition of benzyne has occurred to the more hindered C=N–Se grouping in the heterocycle (5).

The very low-field position of the resonance of H_b in adducts (2f and g) is attributable to deshielding by the

heteroaromatic ring, which lies close to H_{11} , provided the $R^4C=CR^3$ moiety has a *cis*-configuration as in (2a).¹ The adducts (2c and e), in which H_b is less deshielded, may contain *trans*- $R^4C=CR^3$, as reasoned for stereoisomers of adducts (2a)¹ and (3a).² Certainly the magnitude of the coupling constant J_{cd} proves a *trans* configuration in the adduct (2d).

In the proton-decoupled ^{13}C n.m.r. spectrum of the adduct (2b) satellite peaks due to coupling with ^{77}Se

side-chain serves to diminish steric crowding of the various substituents on the butadiene moiety. Details of the molecular geometry of (2b) are given in Table 2. The N-Se bond length (1.83 Å) in (2b) agrees with values reported for compound (1a)⁷ and for 1,2-benzoselenazole.⁸ The heterocyclic C-N bond distance (1.29 Å) is significantly shorter than that in 1,2-benzoselenazole⁸ or than that in pyridine,⁹ and indicates a relatively localised double bond as in formaldoxime (1.276 Å).¹⁰

TABLE 1
 1H N.m.r. data of benzyne adducts (2) ^{a, b}

Compound	R ¹	R ²	R ³	R ⁴	R ⁴ C=CR ³	H _a	H _b	H _d	J _{ab}	J _{ad}	J _{bc}	Mc	J _{HMe}
(2a)	H _a	H _b	H _c	H _d	<i>cis</i>	5.46 ^e	8.28 ^e	<i>c, d</i>	11.1	1.5	11.8		
(2b)	H _a	Me	Me	H _d	<i>cis</i>	5.09 ^e		6.71 ^e		ca. 0		2.13, 2.15	1.6
(2c)	H _a	Me	H _c	H _d	<i>trans</i>	5.69	7.37	7.05 (br)	16.4	0.6		2.36	1.2
(2d)	H _a	Me	H _c	H _d	<i>f</i>	5.35 (br)		7.16 ^g		<1		2.17	1.6
(2e)	Br	H _b	H _c	Br	<i>f</i>		7.41 ^h				12.0		
(2f)	H _a	H _b	Cl	H _d	<i>cis</i>	5.69	8.37	<i>d</i>	12.4	1.5			
(2g)	H _a	H _b	Cl	H _d	<i>trans</i>	6.17	8.78	<i>d</i>	16.3	0.8			
(2h)	H _a	Cl	H _c	H _d	<i>f</i>	5.50		<i>d</i>		1.2			
(2i)	H _a	H _b	benzo		<i>cis</i>	5.39	7.14		12.4				

^a In CDCl₃, δ in p.p.m. downfield from internal SiMe₄, J in Hz. ^b All showed Ar-H multiplets at δ 7.2–8.3. ^c Cf. δ 5.95 (H_a), 7.38 (H_d), and 8.38 (H_b) in (CD₃)₂SO reported in ref. 1. ^d Not resolved from Ar-H. ^e Cf. δ 5.54 (H_a) and 7.01 (H_d) in (CD₃)₂SO; Ar-H assignments in Experimental section. ^f Stereochemistry not assigned. ^g Also δ 7.63 (H_c), J_{cd} 15.5 Hz. ^h Also δ 7.03 (H_c).

($|^1J_{CSe}|$ 129 and $^2J_{CSe}$ 11 Hz) confirm the identity of the hetero-ring carbon atoms at chemical shifts (δ 137, 152, and 163) very similar to those recorded for (2a),¹ but unexpectedly the resonance of another non-protonated carbon atom appears further downfield (δ 166). The isoxazole (3b), prepared for comparison, also showed one carbon resonance (δ 163) downfield of those for the carbonyl groups. By analogy with compound (4a), in which the methyl-substituted carbon resonance is at δ 160, the strongly deshielded carbon atom in (2b) and (3b) must be either C-3 or C-4 of the side-chain (numbering from CN). Of these, C-3 is the more likely because of conjugation with the nitrile group.

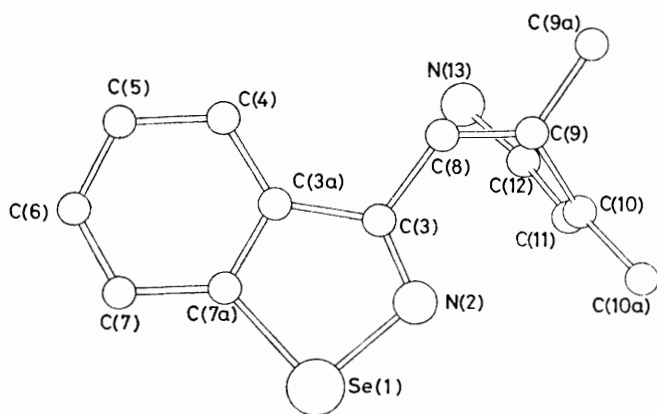


FIGURE The molecular structure of compound (2b) and the atom numbering scheme (hydrogen atoms not shown)

The structure of adduct (2b) was confirmed by X-ray diffraction, which shows a dihedral angle of 84° about the central C-C bond in the side chain (Figure). Examination of molecular models confirms that twisting of the

Although the C-Se-N bond angle (91.0°) found for (2b) is larger than that at selenium in some other five-membered rings,¹¹ it is still smaller than the values (95°) reported for the angle at sulphur in two 1,2-benzothi-

TABLE 2

Molecular geometry of benzyne adduct (2b) with estimated standard deviations in parentheses

Bond lengths (Å)		Bond angles (°)	
Ring atoms			
Se(1)-N(2)	1.833(7)	C(7a)-Se(1)-N(2)	91.0(4)
N(2)-C(3)	1.292(11)	Se(1)-N(2)-C(3)	109.6(6)
C(3)-C(3a)	1.477(13)	N(2)-C(3)-C(3a)	119.8(9)
C(3a)-C(4)	1.413(13)	C(3)-C(3a)-C(7a)	110.3(9)
C(4)-C(5)	1.455(14)	C(3)-C(3a)-C(4)	127.0(10)
C(5)-C(6)	1.458(17)	C(7a)-C(3a)-C(4)	122.6(9)
C(6)-C(7)	1.358(17)	C(3a)-C(4)-C(5)	116.1(11)
C(7)-C(7a)	1.407(14)	C(4)-C(5)-C(6)	118.8(12)
C(7a)-C(3a)	1.424(14)	C(5)-C(6)-C(7)	123.8(11)
C(7a)-Se(1)	1.845(11)	C(6)-C(7)-C(7a)	117.5(12)
		C(7)-C(7a)-C(3a)	121.1(11)
		C(7)-C(7a)-Se(1)	129.5(10)
Side-chain		C(3a)-C(7a)-Se(1)	109.2(7)
C(3)-C(8)	1.476(12)	N(2)-C(3)-C(8)	122.0(9)
C(8)-C(9)	1.351(12)	C(3a)-C(3)-C(8)	118.2(9)
C(9)-C(9a)	1.513(13)	C(3)-C(8)-C(9)	125.2(10)
C(9)-C(10)	1.517(13)	C(8)-C(9)-C(9a)	120.9(10)
C(10)-C(10a)	1.510(14)	C(8)-C(9)-C(10)	124.2(10)
C(10)-C(11)	1.352(13)	C(9a)-C(9)-C(10)	114.9(8)
C(11)-C(12)	1.475(17)	C(9)-C(10)-C(10a)	117.5(10)
C(12)-N(13)	1.145(15)	C(9)-C(10)-C(11)	121.6(11)
		C(10a)-C(10)-C(11)	120.3(11)
		C(10)-C(11)-C(12)	118.9(11)
		C(11)-C(12)-N(13)	176.1(16)

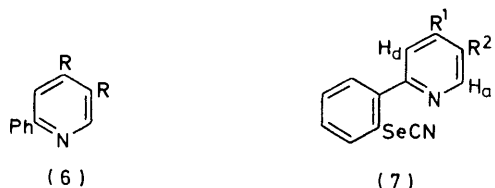
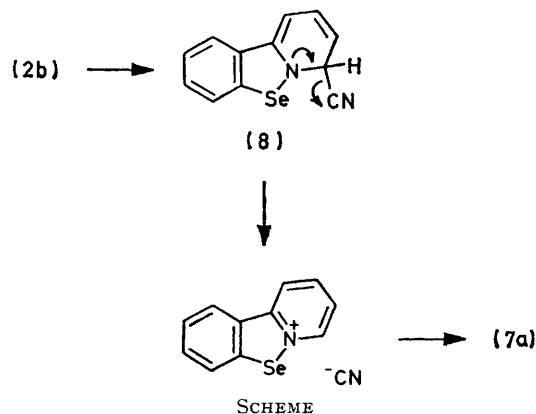
azole derivatives¹² and consistent with the observation that the bond angle at the hetero-atom decreases with increase in atomic number.¹³

U.v. irradiation of adduct (2b) in solution caused its quantitative isomerisation into a new compound C₁₄H₁₂N₂Se. The same transformation occurred on heating (2b) alone or in solution at or above 140 °C.

The i.r. spectrum of the product showed only a very weak absorption at $2\ 132\text{ cm}^{-1}$ in place of the $\text{C}\equiv\text{N}$ absorption at $2\ 220\text{ cm}^{-1}$ for (2b); this is outside the normal range for nitriles,¹⁴ and unlike the strong absorption characteristic of isonitriles.¹⁵ In the mass spectrum of the new compound the molecular-ion peaks were relatively less intense than for (2b), and the base peak ($m/e\ 262.014$) had the composition $\text{C}_{13}\text{H}_{12}\text{N}^{80}\text{Se}$ (calc. $m/e\ 262.014$) corresponding to $M^+ - \text{CN}$ and implicating the presence of a $\text{C}\equiv\text{N}$ grouping of some kind. We therefore formulate the rearranged product as a selenocyanate, ArSeCN ($\text{Ar} = \text{C}_{13}\text{H}_{12}\text{N}$), analogous to some compounds which show i.r. absorption¹⁶ of moderate intensity between $2\ 150$ and $2\ 160\text{ cm}^{-1}$. In the ^{13}C n.m.r. spectrum of our rearranged product the peak assigned to $\text{C}\equiv\text{N}$ ($\delta\ 144$) showed widely spaced satellites due to coupling with ^{77}Se ($|^1J_{\text{CSe}}|\ 244\text{ Hz}$) comparable to that observed for KSeCN in $^2\text{H}_2\text{O}$ ($|^1J_{\text{CSe}}|\ 268\text{ Hz}$).

The ^1H n.m.r. spectrum of the rearranged product showed the singlet resonances for two protons (H_a and H_d) (broadened by unresolved coupling to the methyl groups on the intervening carbon atoms) shifted downfield (to $\delta\ 8.48$ and 8.18) from their positions in (2b), suggesting that the butadiene side-chain of (2b) was now incorporated into an aromatic ring. Computer simulation of the resonances due to the other aromatic protons

(2b) to give the intermediate (8), which could rearrange further *via* an ionic, free radical, or concerted mechanism. Evidence to support an ionic pathway (Scheme) for the rearrangement in refluxing *NN*-dimethylformamide is provided by the formation of silver cyanide (77%) in the presence of dissolved silver nitrate. No



- (6)
 a ; R = Me
 b ; R = Cl
 c ; R = H

- (7)
 a ; R¹ = R² = Me
 b ; R¹ = R² = Cl
 c ; R¹ = Cl, R² = H
 d ; R¹ = H, R² = Cl

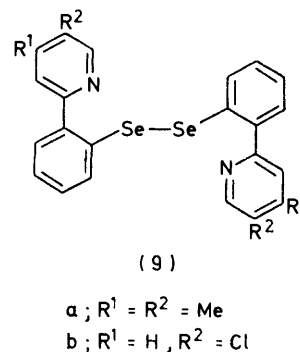
gave values for the chemical shifts and coupling constants (see Experimental section) different from those for (2b) but still consistent with the presence of an *o*-disubstituted benzene ring.

Reductive deselenisation¹⁷ of the rearranged product with Raney nickel replaced the SeCN group by H, and gave an oil, $\text{C}_{13}\text{H}_{13}\text{N}$, which was identified as 4,5-dimethyl-2-phenylpyridine (6a) by comparison of its u.v. absorption with that of 2-phenylpyridine (6c)¹⁸ and of its i.r. spectrum with that reported for (6a),¹⁹ and by preparation of its picrate for m.p. comparison. This evidence allows the assignment of structure (7a) to the rearranged adduct formulated above as ArSeCN . The magnetic deshielding experienced by the protons H_a and H_d is due to their situations, one at the 6-position of the pyridine ring, the other at the 3-position next to the phenyl substituent.

To account for the formation of (7a) we envisage an electrocyclic rearrangement involving the side chain of

silver cyanide was obtained from (7a) and silver nitrate under the same conditions. In another control experiment, the selenocyanate (7a) was found to exchange cyanide with K^{14}CN , so that a random distribution of isotopically labelled cyanide was attained after several minutes in refluxing *NN*-dimethylformamide (*cf.* exchange reported for benzyl selenocyanate²⁰). This result unfortunately invalidated an attempt to obtain further evidence for an ionic mechanism by observing incorporation of radioactive carbon during the rearrangement (2b) \rightarrow (7a) in the presence of K^{14}CN .

There are precedents for the hydrolysis of selenocyanates to selenols, which are oxidised by air to diselenides.²¹ Acidic hydrolysis of the rearranged adduct (7a) afforded in 84% yield a compound recognised as the diselenide (9a) on the basis of analytical and spectro-



- (9)
 a ; R¹ = R² = Me
 b ; R¹ = H, R² = Cl

scopic evidence. In the mass spectrum the molecular-ion peaks are of very low intensity, but stronger peaks appear for the selenide ion $M^+ - \text{Se}$ and the base peak ($m/e\ 262.013$) is due to $\text{C}_{13}\text{H}_{12}\text{N}^{80}\text{Se}$, the same as that for (7a). The same diselenide (9a) was also obtained from the reaction in which the benzyne adduct (2b) was heated

$C_{14}H_{12}N_2Se$ requires C, 58.5; H, 4.2; N, 9.75%; δ_C 166.2 (s), 162.6 (s, C-3), 152.0 (s, C-7a), 143.3 (s), 137.7 (s, C-3a), 127.6, 125.3, 124.9, 124.6, and 119.9 (five d, ring atoms 4—7 and C-8), 116.7 (s, $C\equiv N$), 94.3 (d, C-11), and 22.9 and 22.0 (two q, Me); m/e 290/289/288/287/286/285/284/283 (overlapping multiplets for M^+ and $[M - H]^+$, 4/10/75/90/40/70/15/5%), 273 (20), 271 (15), 264/263/262/261/260/259/258 $[M - CN]^+$, 20/20/100/5/70/20/20), 183 (20), and 103 (30). The low-field region of the 1H n.m.r. spectrum was better resolved in $(CD_3)_2SO$ than in $CDCl_3$; computer-simulation using LAOCOON-3 gave the following parameters for the aromatic hydrogens: δ 8.30 (m, H_c), 8.23 (m, H_b), 7.60 (m, H_f), and 7.54 (m, H_g); J_{ef} 8.2, J_{eg} 1.0, J_{eh} 0.55, J_{fg} 7.1, J_{fh} 1.4, and J_{gh} 8.3 Hz. The methyl hydrogens absorbed as overlapping doublets, δ 2.13 and 2.15, $J(H_aMe) = J(H_dMe) = 1.6$ Hz.

Preliminary cell dimensions and space group data for crystals of (2b) were obtained from rotation and Weissenberg photographs. Accurate unit-cell dimensions were determined by a least-squares refinement of the values of 20 reflections measured on a Hilger and Watts Y290 computer-controlled four-circle diffractometer. Integrated intensities were collected up to $\theta = 60^\circ$ using the ω -scan technique. 1 921 independent reflections were measured, of which 625 with $I < 3\sigma(I)$ were classified as unobserved and not used in the structure determination. Corrections were applied for Lorentz and polarisation factors but not for absorption.

Crystal Data.— $C_{14}H_{12}N_2Se$, $M = 287.2$. Monoclinic, $a = 17.262(3)$, $b = 6.957(1)$, $c = 10.920(2)$ Å, $\beta = 99.61(2)^\circ$, $U = 1 293$ Å³, $Z = 4$, space group $P2_1/a$, Cu- $K\alpha$ radiation, $\lambda = 1.540$ Å.

Structure Analysis.—The structure of (2b) was determined by direct methods using the program MULTAN.²⁸ The positions of Se and 13 light atoms were revealed by an

TABLE 3
Atomic co-ordinates for adduct (2b)^{a, b}

Atom	x/a	y/b	z/c
Se(1)	0.582 9(1)	0.902 8(2)	0.954 7(1)
N(2)	0.567 0(5)	0.738 5(12)	1.079 3(7)
C(3)	0.600 5(6)	0.575 7(14)	1.065 5(8)
C(3a)	0.645 1(6)	0.549 6(16)	0.962 4(9)
C(4)	0.686 6(6)	0.383 9(16)	0.936 1(9)
C(5)	0.725 9(7)	0.395 6(23)	0.829 4(11)
C(6)	0.719 2(8)	0.572 4(25)	0.756 7(10)
C(7)	0.678 5(7)	0.729 3(22)	0.783 8(11)
C(7a)	0.600 5(6)	0.575 7(14)	1.065 5(8)
C(8)	0.594 9(6)	0.411 3(16)	1.149 0(9)
C(9)	0.578 5(6)	0.424 0(15)	1.265 4(9)
C(9a)	0.569 2(8)	0.245 0(17)	1.340 3(9)
C(10)	0.567 0(7)	0.611 8(16)	1.330 6(9)
C(10a)	0.484 0(7)	0.685 3(19)	1.322 8(11)
C(11)	0.626 9(7)	0.698 6(17)	1.406 0(10)
C(12)	0.706 6(10)	0.616 7(20)	1.416 4(10)
N(13)	0.770 1(7)	0.563 6(17)	1.425 5(10)

^a Numbering as in the Figure. ^b Estimated standard deviations ($\times 10^4$) are given in parentheses.

E -map, and a structure-factor calculation on these atoms gave an R value of 0.293; the remaining three light atoms were located by a difference-Fourier map. The structure was refined by full-matrix least-squares methods, initially with isotropic and then with anisotropic thermal parameters, reducing R to 0.103. The atomic co-ordinates for (2b) are given in Table 3. Observed and calculated structure factors and anisotropic thermal parameters are available in Supplementary Publication No. SUP 22936 (10 pp.).*

Benzyne Addition to 5-Methyl-2,1,3-benzoselenadiazole (1c) (4.0 g).—Unreacted (1c) (2.6 g, 65%) was recovered, followed by the 4-methyl-5-(1,2-benzoselenazol-3-yl)pentadienonitrile (2c) (0.66 g, 12%) as glistening yellow crystals, m.p. 144—154 °C (from methanol) (Found: C, 57.4; H, 3.7; N, 10.2). $C_{13}H_{10}N_2Se$ requires C, 57.15; H, 3.7; N, 10.3%; then the 3-methyl isomer (2d) (0.33 g, 6%) as yellow crystals, m.p. 165—171 °C (from methanol) (Found: C, 57.3; H, 3.7; N, 10.5%). The unsharp m.p. of both adducts even after repeated recrystallisation suggests cross-contamination of each by the other, although this was not apparent from their 1H n.m.r. spectra (Table 1). Their i.r. spectra showed some differences, but mass spectra of the two adducts were indistinguishable: m/e 276/275/274/273/272/271/270/269 (overlapping multiplets for M^+ and $[M - H]^+$, 10/22/70/90/45/60/30/18%) and other multiplets 250—243 and 170—164, and 103 (90).

Benzyne Addition to 5-Chloro-2,1,3-benzoselenadiazole (1d) (4.3 g).—First eluted was an unidentified yellow by-product (0.10 g), m.p. 188—192 °C (from benzene) (Found: C, 51.9; H, 2.9; N, 5.4%), i.r. absorption for $C\equiv N$ absent, possibly an impure sample of the diselenide (9b). Next was 2-(4-chloro-2-pyridyl)phenyl selenocyanate (7c) (0.11 g, 2%) as pale yellow microcrystals, m.p. 182—184 °C (from methanol) (Found: C, 49.1; H, 2.5; N, 9.3). $C_{12}H_7ClN_2Se$ requires C, 49.1; H, 2.4; N, 9.5%; ν_{max} 2 137 cm^{-1} ($C\equiv N$); m/e 296/295/294/293/290 (M^+ , 10/5/25/4/12/5/5%) and 270/269/268/267/266/265/264 ($[M - CN]^+$, 56/20/100/18/60/26/24). Next eluted was the 5-chloro-isomer (7d) (0.18 g, 3%), m.p. 166—169 °C (from methanol) (Found: C, 49.3; H, 2.3; N, 9.25%); ν_{max} 2 139 cm^{-1} ($C\equiv N$); mass spectrum almost identical to that of (7c). Further elution recovered unreacted (1d) (3.4 g, 79%), then the *cis*-4-chloro-5-(1,2-benzoselenazol-3-yl)pentadienonitrile (2f) (0.23 g, 4%) as yellow leaflets, m.p. 80—115 °C (from benzene, then from methanol), which was still contaminated with (1d) (t.l.c. and 1H n.m.r. spectrum) even after steam-distillation, re-chromatography, and multiple recrystallisation. A later fraction contained the *trans*-4-chloro-adduct (2g) (10 mg) contaminated with (1d) and (2f), but recognised by additional 1H n.m.r. absorptions (Table 1). Lastly there was obtained a mixture (50 mg) of the isomeric 3-chloro-adduct (2h) (<1%) and unreacted (1d).

Benzyne Addition to 4,7-Dibromo-2,1,3-benzoselenadiazole (1e) (6.8 g).—2,5-Dibromo-5-(1,2-benzoselenazol-3-yl)pentadienonitrile (2e) (0.8 g, 10%) was obtained as needles, m.p. 169 °C (from methanol) (Found: C, 34.4; H, 1.4; N, 6.6). $C_{12}H_6Br_2N_2Se$ requires C, 34.55; H, 1.45; N, 6.7%; m/e 422/421/420/419/418/417/416/415/414/413/412 (M^+ , 2/2/10/3/17/4/15/4/6/2/2%) and other multiplets 341—333, and 260—254 (loss of one and two Br atoms), and 182 (26) and 178 (26). Further elution returned unreacted (1e) (4.1 g, 81% recovery including 1.4 g which was filtered from the reaction mixture before evaporation of the tetrahydrofuran).

Benzyne Addition to 4,7-Dibromo-5,6-dimethyl-2,1,3-benzoselenadiazole (1f) (3.7 g).—This used benzenediazonium-2-carboxylate prepared from anthranilic acid (1.4 g, 10 mmol). Only unreacted (1f) was obtained (1.1 g from the reaction mixture before chromatography and 1.6 g eluted from the column, total recovery 73%).

Benzyne Addition to 5,6-Dichloro-2,1,3-benzoselenadiazole (1g) (5.1 g).—As tetrahydrofuran was evaporated from the

* See Notice to Authors No. 7 in *J.C.S. Perkin 1*, 1979, Index issue.

crude reaction mixture a brown solid precipitated. This was separated and recrystallised from a large volume of benzene to afford 2-(4,5-dichloro-2-pyridyl)phenyl selenocyanate (7b) (4.3 g, 65%) as pale yellow hair-like needles, m.p. 241—244 °C (Found: C, 44.2; H, 2.0; N, 8.8. $C_{12}H_6Cl_2N_2Se$ requires C, 44.0; H, 1.85; N, 8.6%); ν_{max} , 2137 cm^{-1} (C≡N); δ_H (CF₃CO₂H) 9.35 (s, 6-H), 8.72 (s, 3-H), and 8.5—7.7 (4 H, m, other Ar-H); m/e 332/331/330/329/328/327/326/325/324 (M^+ , 4/3/17/6/26/6/13/4/4%) and 306/305/304/303/302/301/300/299/298 ($[M - CN]^+$, 22/18/50/22/100/17/52/20/20). Chromatography of the remaining material returned unreacted (1g) (1.2 g, 23%).

When the benzyne addition was carried out at ca. 40 °C and the same work-up procedure followed, the selenocyanate (7b) (59%) was again obtained and (1g) (25%) recovered. No evidence was found for the presence of the corresponding adduct (11a) of the nitrile series.

Benzyne Addition to 5,6-Dichloro-2,1,3-benzothiadiazole (10b).—The thiadiazole (10b) (67% yield), buff needles, m.p. 109 °C (from methanol) (lit.²⁹ m.p. 109.5—110.0 °C) was prepared from 4,5-dichloro-1,2-phenylenediamine and *N*-sulphonylaniline as described for the analogous dibromo-derivative.³⁰ The general procedure for benzyne addition using (10b) (5.0 g) afforded 3,4-dichloro-5-(1,2-benzothiazol-3-yl)pentadienenitrile (11b) (0.14 g, 2%) as prisms, m.p. 231—232 °C (from methanol) (Found: C, 51.2; H, 1.9; N, 9.7. $C_{12}H_6Cl_2N_2S$ requires C, 51.4; H, 2.2; N, 10.0%); ν_{max} , 2233 cm^{-1} (C≡N). Further elution gave only brown oils from which no further compounds were isolated.

Benzyne Addition to Naphtho[1,2-c][1,2,5]selenadiazole (5) (2.3 g).—This used benzenediazonium-2-carboxylate prepared from anthranilic acid (1.4 g, 10 mmol). The adduct (2i) (30 mg, 1%) was obtained as needles, m.p. 110—112 °C (from methanol) (Found: C, 62.4; H, 3.1; N, 9.4. $C_{16}H_{10}N_2Se$ requires C, 62.1; H, 3.3; N, 9.1%), m/e 312/311/310/309/308/307/306 (M^+ , 15/30/43/100/41/57/30/22%), and 286/285/284/283/282/281/280 ($[M - CN]^+$, 4/15/11/48/11/30/18/15). Further elution gave no more material.

Addition of Dimethyl Acetylenedicarboxylate to 5,6-Dimethyl-2,1,3-benzoxadiazole (10a).—The *N*-oxide of (10a) (4.7 g) [prepared from 4,5-dimethyl-2-nitroaniline (5.0 g) with sodium hypochlorite³¹] in methanol (100 ml) and trimethyl phosphite (20 ml) was heated under reflux for 2 h. The mixture was cooled and poured into ice-water; the precipitate was collected and recrystallised to give (10a) (3.6 g, 73%), m.p. 84—85 °C (from ethanol) (lit.³² 83—85 °C). Dimethyl acetylenedicarboxylate (4.3 g) and (10a) (2.7 g) in dichloromethane (110 ml) were irradiated for 12 h. After evaporation of dichloromethane the brown residue was chilled and the resulting solid recrystallised to give 3,4-dimethyl-5-(4,5-bismethoxycarbonyl-1,2-oxazol-3-yl)pentadienenitrile (3b) (5.4 g, 93%), m.p. 84 °C (from light petroleum, b.p. 60—80 °C) (Found: C, 57.9; H, 4.8; N, 9.7. $C_{14}H_{14}N_2O_5$ requires C, 57.9; H, 4.9; N, 9.6%); ν_{max} , 2220 (C≡N), 1738 and 1715 (C=O) cm^{-1} ; δ_H 6.68 and 5.26 (each 1 H, q, J_{HMe} 1.8 Hz, CH), 4.10 and 4.00 (each 3 H, s, OMe), and 2.17 and 2.12 (each 3 H, d, Me); δ_C 163.6 (s, C-4 or C-3), 160.6 and 160.4 (two s, C=O), 157.6 and 156.8 (two s, C-3' and C-5'), 146.1 (s, C-3 or C-4), 116.1 (s, C-4'), 114.1 (s, C≡N), 112.7 (d, C-5), 95.9 (d, C-2), 53.4 and 52.8 (two q, OMe), and 23.3 and 22.2 (two q, Me); m/e 290 (M^+ , 15%), 231 ($[M - CO_2Me]^+$, 60), 199 (100), and 131 (45); m^* 184.0 (290 → 231), 171.4 (231 → 199), and 86.2 (199 → 131).

The adduct (3b) was recovered unchanged after being

heated in refluxing toluene for 1 h or alone at 250 °C for 1 h or after further u.v. irradiation in dichloromethane.

Rearrangement of the Benzyne Adduct (2b).—U.v. irradiation of the adduct (2b) (200 mg) in dichloromethane (100 ml) for 24 h afforded 2-(4,5-dimethyl-2-pyridyl)phenyl selenocyanate (7a) (193 mg, 97%), m.p. 169—172 °C (from methanol) (Found: C, 58.4; H, 4.3; N, 9.7. $C_{14}H_{12}N_2Se$ requires C, 58.5; H, 4.2; N, 9.75%); λ_{max} (EtOH) 249, 267sh, 296, 305sh and 348sh nm (ϵ 1 950, 1 390, 950, 670, and 20 $m^2 mol^{-1}$); ν_{max} , 2132 cm^{-1} (C≡N); δ_H [(CD₃)₂SO] 8.48 and 8.18 (each 1 H, s, H_a and H_d), 2.38 and 3.20 (each 3 H, s, Me), and Ar-H analysed by computer simulation, 8.33 (1 H, m, H_e), 8.06 (1 H, m, H_h), 7.56 (2 H, m, H_f and H_g) (J_{ef} 7.8, J_{eg} 2.3, J_{eh} 0.5, J_{fg} 7.1, J_{fh} 0.7, and J_{gh} 9.3 Hz); δ_C 150.6 (s), 148.0 (s), 143.7 (d), 133.8 (s), 132.0 (s), 130.8 (d), 129.9 (d), 128.0 (s), 127.1 (d), 126.0 (d), and 119.6 (d) (aromatic ring C), 112.0 (C≡N), and 19.8 and 16.3 (two q, Me); m/e 290/289/288/287/286/285/284 (M^+ , 4/4/15/1/10/3/8%), 264/263/262/261/260/259/258 ($[M - CN]^+$, 15/15/100/8/63/40/82), 208 (80), and 207 (50).

Another sample of the adduct (2b) (50 mg) was heated at 140 °C for 10 min, cooled, and recrystallised from methanol to give the selenocyanate (7a) (47 mg, 94%), identical by i.r. spectrum, m.p., and mixed m.p. with the material obtained above. Recrystallisation of (2b) from *NN*-dimethylformamide, mesitylene, or xylene, in each case by heating to the b.p. for several minutes, also afforded (7a) on cooling (ca. 90%).

The adduct (2b) (100 mg) and silver nitrate (300 mg) in *NN*-dimethylformamide (20 ml) were stirred and heated under reflux for 0.5 h. The hot mixture was filtered from silver cyanide [36 mg, 77% based on (2b)], which was confirmed by dissolving in dilute nitric acid and conversion into Prussian Blue. The filtrate was cooled and diluted with water; the brown precipitate was collected and recrystallised to give the diselenide (9a) (47 mg, 52%) as rods, m.p. 211—213 °C (from methanol) (Found: C, 60.0; H, 4.3; N, 5.3. $C_{26}H_{24}N_2Se_2$ requires C, 59.8; H, 4.6; N, 5.4%); λ_{max} (CH₂Cl₂) 350 nm (ϵ 1 330 $m^2 mol^{-1}$); ν_{max} , C≡N absent; m/e 446/445/444/443/442/441/440 ($[M - Se]^+$, 1/1/4/1/2/1/1%), 264/263/262/261/260/259/258 ($C_{13}H_{12}NSe^+$, 25/40/100/30/60/30/25), 183 (25), and 182 (22).

In another experiment the selenocyanate (7a) was heated with silver nitrate in refluxing *NN*-dimethylformamide for 0.5 h. No silver cyanide precipitated, and (7a) was recovered (>90%) on cooling.

U.v. Irradiation and Rearrangement of Other Benzyne Adducts (2c—f).—The adducts (2c and d) (each 100 mg) in dichloromethane (100 ml) were separately irradiated until, after 6 h, t.l.c. analysis showed the disappearance of starting material. Evaporation of the solvent left a brown tarry residue which was chromatographed on alumina. Ether eluted discoloured semi-crystalline material containing the corresponding selenocyanates, ν_{max} (CHCl₃) 2140 cm^{-1} , conjugated C≡N absent, which could not be satisfactorily purified.

The adducts (2e and i) were recovered unchanged (>90%) after u.v. irradiation of each separately in dichloromethane for 48 h.

U.v. irradiation of the adduct (2f) contaminated with unreacted (1d) (200 mg) in dichloromethane (100 ml) for 24 h, followed by evaporation of the solvent and chromatography of the residue, afforded the selenocyanate (7c) (115 mg, 60%), m.p. 181—184 °C, identical in respect of i.r. spectrum and mixed m.p. with the sample obtained from

benzyl addition to (1d). A later column fraction returned (1d) (10 mg).

Deselenisation of the Selenocyanates (7a and b).—Rearranged adduct (7a) (100 mg) in benzene (10 ml) and ethanol (2 ml) was stirred and heated under reflux with Raney nickel³³ (ca. 2 g) for 6 h. The solid was filtered and washed with benzene. Filtrate and washings were combined and shaken with concentrated sulphuric acid (2 × 10 ml) and then with water (2 × 10 ml). The benzene layer was separated, dried, and evaporated, and the residue was distilled at 130 °C (bath)/2 mmHg to give 4,5-dimethyl-2-phenylpyridine (6a) (48 mg, 86%) as a pale straw-coloured oil (Found: C, 84.7; H, 6.9; N, 7.9. Calc. for C₁₃H₁₃N: C, 85.2; H, 7.2; N, 7.6%); λ_{max} (EtOH) 246 and 275 nm (ε 1110 and 824 m² mol⁻¹) [cf. (6c)¹⁸], i.r. spectrum in agreement with that reported previously; ¹⁹m/e 183 (M⁺, 100%), 182 ([M - H]⁺, 25), and 168 ([M - Me]⁺, 11); m* 181 (183 → 182) and 154 (183 → 168); picrate, m.p. 203—204 °C (from ethanol) (lit.¹⁹ 202—203 °C).

The selenocyanate (7b) (0.50 g) in benzene-ethanol was treated with Raney nickel (ca. 10 g) and worked up as described above. Removal of the solvent left a pink oil which solidified on chilling. Recrystallisation from methanol below 0 °C afforded 4,5-dichloro-2-phenylpyridine (6b) (0.28 g, 83%), m.p. 57—59 °C (Found: C, 59.2; H, 3.3; N, 6.2. C₁₁H₇Cl₂N requires C, 59.2; H, 3.2; N, 6.3%); δ_H 8.66 and 7.80 (each 1 H, s, 6- and 3-H), 8.0—7.9 (2 H, m Ar-H) and 7.6—7.2 (3 H, m, Ar-H); m/e 227/226/225/224/223/222 (M⁺, 10/9/67/20/100/12%) and 190/189/188 ([M - Cl]⁺, 11/9/40); m*, 158.5 (223 → 188).

Hydrolysis of the Selenocyanates (7a and d).—The selenocyanate (7a) (100 mg) in water (4 ml), ethanol (6 ml), and concentrated hydrochloric acid (2 ml) was heated at 90 °C for 12 h. The solution was cooled and extracted with chloroform; the extract was dried (MgSO₄) and the solvent evaporated, leaving an oil which solidified after several hours. Recrystallisation from methanol afforded the diselenide (9a) (76 mg, 84%), m.p. 211—213 °C, identical in respect of i.r. spectrum and mixed m.p. with the sample obtained from (2b) in the presence of silver nitrate.

The selenocyanate (7d) (50 mg) dissolved on being heated in ethanol (5 ml), water (2 ml), and concentrated hydrochloric acid (1 ml). After 12 h at 100 °C the solution was cooled and extracted with chloroform; the extract was dried (MgSO₄) and evaporated to give 2-(5-chloro-2-pyridyl)-phenyl diselenide (9b) (41 mg, 92%) as hair-like needles, m.p. 260—262 °C (from methanol) (Found: C, 49.1; H, 2.4; N, 4.8. C₂₂H₁₄Cl₂N₂Se₂ requires C, 49.4; H, 2.6; N, 5.2%); i.r. absorption for C≡N absent; ¹H n.m.r. spectrum of poor quality because of low solubility; m/e M⁺ absent, multiplets 460—452 ([M - Se]⁺), 307—299 (all < 5%), 272/271/270/269/268/267/266/265/264 (C₁₁H₇ClNSe⁺, 5/5/45/15/100/15/50/18/18), and 235/234/233/232/231/230/229/228 (C₁₁H₇NSe⁺, 4/5/20/12/11/9/6/3); m* 201br (456 → 303).

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