Reactions of 2,1,3-Benzoselenadiazole and 2,1,3-Benzothiadiazole with Benzyne and Dimethyl Acetylenedicarboxylate

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Two 1 : 1 adducts obtained from benzyne and 2,1,3-benzoselenadiazole are stereoisomeric 5-(1,2-benzoselenazol-3-yl)penta-2,4-dienonitriles (12a and b). With dimethyl acetylenedicarboxylate 2,1,3-benzoselenadiazole affords dimethyl quinoxaline-2,3-dicarboxylate and selenium. The corresponding products are obtained in lower yields from addition reactions of 2,1,3-benzothiadiazole.

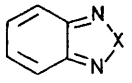
A PREVIOUS paper by two of us [1] described the reaction of benzyne with 2-alkylbenzotriazoles (1) to give 1-phenylbenzotriazole and noted the formation of 1 : 1 adducts of benzyne with the related heterocycles (3) and (4). We have now characterised these adducts, for which no structures were given before, and have observed contrasting patterns of cycloaddition of (3) and (4) with benzyne and with dimethyl acetylenedicarboxylate, respectively.

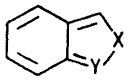
Cycloaddition of dienophiles across the 1- and 3-posi-

[1] C. D. Campbell and C. W. Rees, *J. Chem. Soc.* (*C*), 1969, 748.

tions of the heterocycle in derivatives of structures (5)—(7) are well established,[2-4] and the formation of acridine from anthranil (8) and benzyne probably involves a similar reaction.[1] In contrast, although cycloadditions to acyclic heterodienes N=C–C=N are known,[5,6] no examples involving the 1- and 3-positions of the heterocyclic systems (1)—(4) have yet been reported.

Both compounds (3) and (4) fail to add maleic anhydride,[7] and the related naphthothiadiazole (9) reacts instead, like anthracene, across the middle ring.[8] However, from 2,1,3-benzoselenadiazole (4) and dimethyl





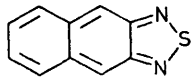
(1) X = NMe, NCH_2Ph
(2) X = O
(3) X = S
(4) X = Se

(5) X = NR, Y = CH
(6) X = O, Y = CH
(7) X = S, Y = CH
(8) X = O, Y = N

acetylenedicarboxylate at 70 °C we obtained the quinoxaline-2,3-diester (11) and selenium (38 and 41% yield, respectively). Both these products are presumably derived from an intermediate 1 : 1 adduct (10). Reaction at room temperature was induced by u.v. irradiation, when (11) and selenium were again obtained. The same diester (11) was obtained in only trace amounts from 2,1,3-benzothiadiazole (3) and the acetylene ester at 100 °C.

Benzyne, generated either by oxidation of 1-aminobenzotriazole with lead tetra-acetate [9] or by decomposition of benzenediazonium-2-carboxylate,[10] in the presence of an excess of 2,1,3-benzoselenadiazole (4), was efficiently trapped to give a mixture of isomeric 1 : 1 adducts, $C_{12}H_8N_2Se$ (88% yield). Chromatography and careful fractional sublimation separated the major adduct, m.p. 140—141 °C, and the minor adduct, m.p. 160—161 °C; the latter (only 0.5% yield) is possibly an artefact of the chromatographic work-up. Benzyne was trapped less efficiently (5—10%) by 2,1,3-benzothiadiazole (3) under the same conditions, and only a single adduct, $C_{12}H_8N_2S$, m.p. 155—156 °C, was isolated in a pure state.

All three of these adducts showed i.r. absorption at 2 220 cm^{-1} indicative of a conjugated C≡N group. The ^1H n.m.r. spectrum of the major adduct from 2,1,3-benzoselenadiazole (4) consisted of overlapping resonances from two independent sets each of four protons; these were better separated in the spectrum in $(CD_3)_2SO$ than in $CDCl_3$. The spectrum was analysed by computer-simulation using LAOCOON-3, from which chemical shifts (δ values) and coupling constants were obtained. One set of four resonances (H_e 8.39, H_f 7.65, H_g 7.58, and H_h 8.24; J_{ef} 8.22, J_{eg} 1.11, J_{eh} 0.75, J_{fg} 7.08, J_{fh} 1.05, and J_{gh} 8.34 Hz) is clearly consistent with hydrogen atoms on an unsymmetrically *ortho*-disubstituted benzene ring; the coupling constants are similar to those reported for 2-methyl-1,3-benzoselenazole or benzo[*b*]selenophen.[11] The second set of four resonances (H_a 5.95, H_b 8.38, H_c 6.96, and H_d 7.38; J_{ab} 11.10, J_{ac} −1.08, J_{ad} 1.46, J_{bc} 11.77, J_{bd} −0.39, and J_{cd} 11.46 Hz) is suggestive of a butadiene moiety with different end-groups,[12] and it is similar to the spectrum of the isoxazole derivative (17a).[13] Taken together, this evidence implies a structure ArCH=CH–CH=CH–CN for the adduct, in which Ar is a benzoselenazolyl group attached through the carbon atom of the hetero-ring. In particular, the relatively high field position of the resonance of H_a identifies this as the hydrogen atom adjacent to the nitrile group; the values of J_{ab} and J_{cd} show that both double bonds in the side chain are *cis*-disubstituted; [12] the existence of five-bond coupling ($J_{ad} > 0$) requires that the whole side chain is



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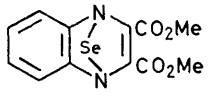
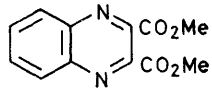


(10)



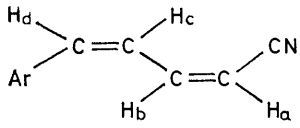
(11)

coplanar; [14] and the magnitude of J_{bc} shows that the 3,4-bond is s-*trans*.[15] Furthermore, the low field position of the resonance of H_b is a result of deshielding by the heteroaromatic ring [structure (a)]. The adduct from benzyne and 2,1,3-benzothiadiazole (3) must contain the same part-structure (a), since its ^1H n.m.r. spectrum was entirely similar.

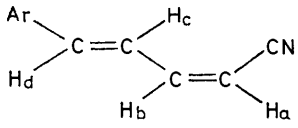
U.v., i.r., and mass spectra of the minor adduct from benzyne and 2,1,3-benzoselendiazole (4) were very like those of the major adduct. In the ^1H n.m.r. spectrum

[2] L. J. Kricka and J. M. Vernon, *J.C.S. Perkin I*, 1972, 904; *Adv. Heterocyclic Chem.*, 1974, **16**, 87, and references therein.
[3] G. Wittig, E. Knauss, and K. Niethammer, *Annalen*, 1960, **630**, 10.
[4] M. P. Cava and N. M. Pollack, *J. Amer. Chem. Soc.*, 1966, **88**, 4112; M. P. Cava and J. P. Van Meter, *J. Org. Chem.*, 1969, **34**, 538; B. Iddon, *Adv. Heterocyclic Chem.*, 1972, **14**, 331, and references therein.
[5] R. Pfleger and A. Jäger, *Chem. Ber.*, 1957, **90**, 2460; S. B. Needleman and M. C. Chang Kuo, *Chem. Rev.*, 1962, **62**, 405.
[6] M. Lora-Tamayo and J. L. Soto, in ' 1,4-Cycloaddition Reactions,' ed. J. Hamer, Academic Press, New York, 1967, p. 179, and references therein.
[7] L. F. Efros and Z. V. Todres-Selektor, *J. Gen. Chem.* (*U.S.S.R.*), 1957, **27**, 1064.
[8] M. P. Cava and R. H. Schlessinger, *Tetrahedron Letters*, 1964, 3815.
[9] C. D. Campbell and C. W. Rees, *J. Chem. Soc.* (*C*), 1969, 742.
[10] F. M. Logullo, A. H. Seitz, and L. Friedman, *Org. Synth.*, 1968, **48**, 12.
[11] F. L. Tobiason and J. H. Goldstein, *Spectrochim. Acta*, 1967, **23A**, 1385; G. Llabrès, M. Baiwir, J. Denoel, J. L. Piette, and L. Christiaens, *Tetrahedron Letters*, 1972, 3177.
[12] *Cf.* ^1H n.m.r. spectra of 1,4-dicyanobutadienes, J. A. Elvidge and P. D. Ralph, *J. Chem. Soc.* (*C*), 1966, 387; J. H. Hall and E. Patterson, *J. Amer. Chem. Soc.*, 1967, **89**, 5856; T. Kajimoto, H. Takahashi, and J. Tsuji, *J. Org. Chem.*, 1976, **41**, 1389.
[13] I. Yavari, S. Esfandiari, A. J. Mostashari, and P. W. W. Hunter, *J. Org. Chem.*, 1975, **40**, 2880.
[14] A. A. Bothner-By and R. K. Harris, *J. Amer. Chem. Soc.*, 1965, **87**, 3451.
[15] J. P. Dorie, M. L. Martin, S. Odiot, and F. Tonnard, *Org. Magnetic Resonance*, 1973, **5**, 265, and references therein.

the resonance of H_b was shifted considerably upfield and that of H_c downfield from their previous positions. Complete analysis of the spectrum was more difficult because of the similarity in chemical shift of H_b, H_c, and H_d. However, the resonance of H_a (5.95) was still upfield from the others owing to shielding by the nitrile group, and its coupling (J_{ab} 10.2 Hz) shows a *cis*-configuration of the 2,3-bond. The changes in chemical shift of H_b and H_c are consistent with a *trans*-configuration of the 4,5-bond, which removes H_b from the magnetic influence of the



(a) *cis, cis* side chain



(b) *cis, trans* side chain

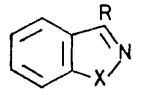
aromatic system [structure (b)]. A similar argument was invoked to assign the structure of compound (17b).[13]

In the ^{13}C n.m.r. spectrum of the major adduct from benzyne and 2,1,3-benzoselenadiazole (4) four resonances can be identified as those of the carbon atoms of CH–CH=CH–CN (δ 129, 147, 102, and 117, respectively) on analogy with assignments made for compound (17a).[13] Only one carbon atom (δ 153) appears strongly coupled to ^{77}Se ($|^1J_{CSe}|$ 129 Hz).[16] The resonance at lowest field (δ 163) assigned to the ring C=N shows a smaller coupling ($|^2J_{CSe}|$ 12 Hz), as does the 3a-bridgehead carbon (δ 138, $|^2J_{CSe}|$ 11 Hz). This favours the 1,2-benzoselenazole structure (12) rather than the 1,3-system (15), but a more reliable distinction between these possibilities followed from chemical degradation.

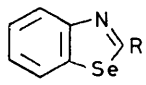
The major adduct (12a) or (15a) retained selenium on being heated with Raney nickel and resisted hydrogenation over palladium–charcoal. Treatment with hot dilute acid or alkali caused incomplete conversion into the *cis-trans*-isomer (b). No identified products were obtained from oxidation with potassium permanganate under acidic or alkaline conditions. However, ozonolysis below −50 °C afforded the known 1,2-benzoselenazole-3-carbaldehyde (13),[17] which is clearly differentiated by m.p. from the isomeric aldehyde (16).[18] An unexpected product from ozonolysis at 0—15 °C was *o*-chlorobenzoic acid. Its formation is also consistent with degradation of the 1,2-benzoselenazole ring system; the chlorine atom must be derived from solvent chloroform, but the mechanism of its incorporation is unknown.

The 1 : 1 adduct of benzyne and 2,1,3-benzoselenadiazole (4) therefore has structure (12a), in agreement with the results of an *X*-ray crystallographic study of a dimethyl derivative.[19] The analogous formulation of the 1 : 1 adduct derived from 2,1,3-benzothiadiazole (3) is (14a). When compound [$^2H_4$]-(4) was used as a trap for benzyne, the ^1H n.m.r. spectrum of the corresponding adduct [$^2H_4$]-(12a) showed only the set of resonances from four aromatic hydrogens. This proves that the side-chain in structure (12) is derived by opening of the benzene ring initially present in (4); it excludes the possibility that (12) is formed *via* a symmetrical intermediate, for example the benzyne adduct analogous to structure (10). The mixture of 1 : 1 adducts obtained from 4-methylbenzyne (generated from 1-amino-5-methylbenzotriazole and lead tetra-acetate) and 2,1,3-benzoselenadiazole (4) was inseparable by chromatography; two ^1H resonances for methyl groups [δ($CDCl_3$) 2.54 and 2.57] implied the presence of both 5- and 6-methyl derivatives of structure (12).

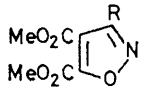
There is a close analogy between the structures (12) and (17), the latter being the adduct (*cis,cis*, *cis,trans*, and *trans,trans* geometrical isomers) obtained photochemically from benzofurazan (2) and dimethyl acetylenedicarboxylate *via* the nitrile oxide intermediate (18).[13] However, an analogous mechanism of formation of (12a), requiring cycloaddition of benzyne to the 1,3-dipolar nitrile selenide (19), can be discounted for the following reasons. A nitrile selenide is expected * to fragment even more readily than nitrile sulphides.[20,21] It is inconceivable that benzyne, itself short-lived, should capture another transient intermediate (19) with nearly 90% efficiency. Also, the formation of the adduct (12a) does not require photochemical excitation of (4). Lastly, the formation of compound (11) rather than an adduct analogous to (17) from 2,1,3-benzoselenadiazole (4) and



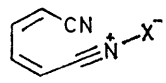
(12) X = Se, R = CH=CH·CH=CH·CN
(13) X = Se, R = CHO
(14) X = S, R = CH=CH·CH=CH·CN



(15) R = CH=CH·CH=CH·CN
(16) R = CHO



(17) R = CH=CH·CH=CH·CN



(18) X = O
(19) X = Se

* Benzonitrile selenide has recently been identified by spectroscopic evidence and shown to decompose above 100 K into benzonitrile and selenium; it would not be trapped with dimethyl acetylenedicarboxylate (C. L. Pedersen and N. Hacker, *Tetrahedon Letters*, 1977, 3981).

[16] *cf.* Values given by W. McFarlane and D. S. Rycroft, *J.C.S. Chem. Comm.*, 1973, 10. The sign of the C–Se coupling constant through one bond is negative, and through two bonds positive.

[17] R. Weber and M. Renson, *J. Heterocyclic Chem.*, 1975, **12**, 1091.

[18] F. M. Hamer, *J. Chem. Soc.*, 1952, 3197.

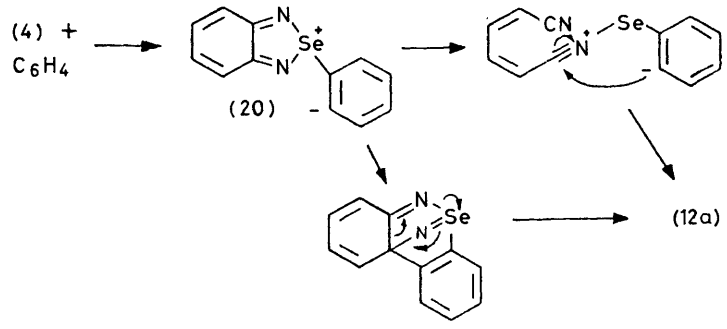
[19] M. R. Bryce and C. D. Reynolds, unpublished work.

[20] H. Gotthardt, *Tetrahedron Letters*, 1971, 1277; *Chem. Ber.*, 1972, **105**, 188.

[21] R. K. Howe and J. E. Franz, *J.C.S. Chem. Comm.*, 1973, 524; *J. Org. Chem.*, 1974, **39**, 962; R. K. Howe, T. A. Gruner, and J. E. Franz, *ibid.*, 1977, **42**, 1813.

dimethyl acetylenedicarboxylate is inexplicable in terms of a nitrile selenide intermediate (19). An alternative mechanism to account for the formation of the adduct (12a) involves initial attack of benzyne at the selenium atom in (4), followed by reorganisation in one or more steps of an intermediate (20). Two possible routes are outlined in the Scheme.

The mechanism suggested [1] to account for the formation of 1-phenylbenzotriazole from benzyne and 2-alkylbenzotriazoles (1) involved oxidative dealkylation by lead tetra-acetate. We therefore hoped to change the course of this reaction by using an alternative source of benzyne. The decomposition of benzenediazonium-2-carboxylate in the presence of 2-methylbenzotriazole gave no detectable 1-phenylbenzotriazole, but phenazine (2% yield) instead. (Phenazine itself also reacts with benzyne to give unidentified coloured products.[1]) The loss of the NMe group in this case is reminiscent of other instances of deamination accompanying additions of benzyne or dimethyl acetylenedicarboxylate.[22]



SCHEME

EXPERIMENTAL

U.v. spectra were recorded for solutions in ethanol and ε values are expressed in m^2 mol^{-1}. I.r. spectra were recorded for Nujol mulls and calibrated with polystyrene. ^1H N.m.r. spectra were recorded at 60 or 100 MHz for solutions in [$^2H_6$]dimethyl sulphoxide and ^{13}C n.m.r. spectra at 15 MHz in [^2H]chloroform; chemical shifts are quoted downfield from internal tetramethylsilane. Tetrahydrofuran (THF) was dried before use. Light petroleum was the fraction having b.p. 40—60 °C.

Reaction of 2,1,3-Benzoselenadiazole (4) *with Dimethyl Acetylenedicarboxylate.*—(i) A solution of (4) (1.83 g) and the acetylene ester (2.84 g) in dichloromethane (100 ml) was irradiated with a Hanovia medium-pressure mercury arc lamp in a water-cooled Pyrex jacket. After 60 h the mixture was filtered from selenium (59 mg, 7.5%) and the filtrate was concentrated. Addition of light petroleum precipitated dimethyl quinoxaline-2,3-dicarboxylate (11) (146 mg, 6%), obtained as buff needles, m.p. 131—132 °C (from methanol) (lit.,[23] 130 °C) (Found: C, 58.7; H, 4.1; N, 11.2. Calc. for $C_{12}H_{10}N_2O_4$: C, 58.5; H, 4.1; N, 11.4%), identical (i.r. spectrum and mixed m.p.) with an authentic specimen.[23] The remaining material was chromatographed on alumina to give unchanged (4) (1.46 g, 81%).

(ii) Almost no reaction occurred between (4) and dimethyl acetylenedicarboxylate in benzene during 1 month at room temperature. The mixture was heated at 70 °C for 10 days and then filtered from selenium (41%). The filtrate was evaporated and the residue was chromatographed on silica, from which benzene eluted unchanged (4) and ether eluted the quinoxaline ester (11) (38%), m.p. 132—132.5 °C, identical with the sample described above.

Reaction of 2,1,3-Benzothiadiazole (3) *with Dimethyl Acetylenedicarboxylate.*—Compound (3) (1.2 g) and the acetylene ester (2.5 g) in toluene were heated at 100 °C for 10 days. The mixture was evaporated and the residue chromatographed on silica, from which benzene eluted unchanged (3), and ether subsequently eluted a yellow oil. T.l.c. (benzene; silica) of the latter showed a spot (R_F 0.5) appropriate for compound (11). The oil was subjected to short-path distillation at 120 °C and 0.01 mmHg, and the distillate on trituration with ether gave (11) (2 mg), m.p. 128—130 °C, identical by t.l.c. with authentic material.

Benzyne Addition to 2,1,3-Benzoselenadiazole (4).—(i) Benzenediazonium-2-carboxylate [10] [from anthranilic acid (1.37 g, 10 mmol)] as a suspension in THF was added over 1 h to 2,1,3-benzoselenadiazole (4) (3.7 g, 20 mmol) in THF (150 ml), which was stirred and heated under reflux during this addition and for a further 0.5 h. The mixture was evaporated onto chromatographic alumina, which was then made into a column and eluted with light petroleum to recover unchanged (4) (1.6 g, 43%). Further elution with light petroleum–ether (9 : 1 v/v) afforded cis,cis-5-(1,2-*benzoselenazol-3-yl*)*penta-2,4-dienonitrile* (12a) (2.3 g, 88% based on benzyne precursor), yellow needles, m.p. 140—141 °C (from ethanol) (Found: C, 55.4; H, 3.3; N, 10.7. $C_{12}H_8N_2Se$ requires C, 55.6; H, 3.1; N, 10.8%), $\lambda_{max.}$ 239, 276, and 357 nm (log ε 3.50, 3.30, and 3.11), $\nu_{max.}$ 2 220 (C≡N), 1 588, 1 412, 1 290, 1 270, 1 170, 812, and 745 cm^{-1}, δ_C 125—128 (carbon atoms bearing H_d, H_e, H_f, H_g, and H_h) and others assigned in the Discussion section; *m/e* 262/261/260/259/258/257/256/255 (M^+ overlapping with M − 1 peaks reflecting Se isotope distribution, 6/15/70/100/35/60/20/20%), 236/235/234/233/232/231/230 (18/18/90/18/65/20/24), 207 (10), 156 (10), 154 (20), 127 (15), 117 (15), 115 (12), and 103 (30).

Continued elution with the same solvent system gave the cis,trans-*adduct* (12b) (0.10 g, 0.5%), yellow needles, m.p. 160—161 °C (from ethanol) (Found: C, 55.3; H, 3.3; N, 10.9%) showing u.v., i.r., and mass spectra very similar to those of the adduct (12a) with, additionally, $\nu_{max.}$ 995 and 980 cm^{-1} (*trans*-CH=CH), δ_H 5.95 (1 H, d J_{ab} 10 Hz, H_a),

[22] L. J. Kricka and J. M. Vernon, *J.C.S. Perkin I*, 1973, 766.

[23] R. A. Baxter and F. S. Spring, *J. Chem. Soc.*, 1945, 229.

7.2—7.9 (5 H, m, H_b, H_c, H_d, H_f, and H_g), 8.2—8.5 (2 H, m, H_e and H_h). Careful fractional sublimation prior to recrystallisation was required to separate (12b) cleanly from (12a). The mass spectrum of analytically pure (12b) showed contamination with another selenium-containing compound, *m/e* 335/334/333/332/331/330/329 (all <5%).

The analytically pure adduct (12a) gave three spots on t.l.c. (R_F 0.38, 0.47, and 0.58 in benzene on alumina); subsequent elution at right angles resolved the second spot into two and the third spot into three with the same R_F values as before. Adduct (12b) gave two spots identical with the slower moving components from (12a). This behaviour suggests that isomerisation occurs on the t.l.c. plate, and we assign the spot of lowest R_F value to the *trans,trans*-isomer which was not isolable in quantity.

(ii) Benzyne was generated *in situ* by dropwise addition of anthranilic acid (1.37 g, 10 mmol) and isopentyl nitrite, separately dissolved in THF, to a refluxing solution of 2,1,3-benzoselenadiazole (4) (3.7 g, 20 mmol) in THF. Work-up and subsequent chromatography on alumina as described above gave unchanged (4) (2.4 g, 66%), the adduct (12a) (0.51 g, 20%), and smaller amounts of anthranilic and benzoic acids, identified by mixed m.p. comparison with authentic samples.

An alternative work-up involved addition of aqueous sodium hydroxide to the crude mixture, which was then extracted with ether. The extract was dried and evaporated. The residue was extracted with benzene and filtered; addition of carbon tetrachloride to the filtrate precipitated acridone (0.1 g), identified by its blue fluorescence in solution and by comparison of m.p. and i.r. [$\nu_{max.}$ 1 640 cm^{-1} (C=O)] and mass spectra [*m/e* 195 (M^+, 100%)] with those of an authentic sample.[24] The formation of acridone as a by-product of benzyne addition to anthranilic acid has been noted before.[25] The adduct (12a) was again isolated by chromatography of the remainder of the product mixture.

(iii) *o*-Phenylenediamine dihydrochloride was recrystallised twice from D_2O after 24 h in refluxing D_2O under nitrogen. This deuteriated material with aqueous selenous acid afforded [$^2H_4$]-2,1,3-benzoselenadiazole, m.p. 73—74 °C (lit.,[26] 75 °C), which showed no detectable ^1H n.m.r. absorptions. Benzyne addition to [$^2H_4$]-(4) by method (ii) gave the adduct [$^2H_4$]-(12a) (32%), m.p. 139—141 °C, identical with previous samples except for its ^1H n.m.r. and mass spectra.

(iv) Lead tetra-acetate (3.1 g, 7 mmol) was added to a solution of 2,1,3-benzoselenadiazole (4) (4.4 g, 24 mmol) in dry benzene (50 ml). This mixture was stirred during dropwise addition of 1-aminobenzotriazole [9] (0.8 g, 6 mmol) in dry benzene. Lead diacetate was filtered off. Benzene was evaporated from the filtrate, and the residue was steam-distilled to remove unchanged (4) (2.9 g, 66%). The residue from steam distillation was extracted with ether and with chloroform; the combined extracts were dried and evaporated onto chromatographic alumina, from which light petroleum–ether eluted the adducts (12a and b) (1.3 g, 85% based on benzyne precursor). The minor adduct (12b) in later fractions of eluate was mixed with (12a), but a pure sample was obtained by fractional sublimation *in vacuo*.

4-Methylbenzyne Addition to 2,1,3-*Benzoselenadiazole* (4).—Oxidation of 1-amino-5-methylbenzotriazole [9] with lead tetra-acetate in dichloromethane in the presence of a four-fold excess of 2,1,3-benzoselenadiazole (4) and work-up as described in method (iv) afforded unchanged (4) (74%) and a mixture of adducts, 5- and 6-methyl derivatives of (12) (98%), m.p. 93—150 °C (Found: C, 57.3; H, 3.8; N, 10.2. Calc. for $C_{13}H_{10}N_2Se$: C, 57.1; H, 3.7; N, 10.3%), $\nu_{max.}$ 2 220 cm^{-1} (C≡N), inseparable by chromatography or fractional crystallisation.

Benzyne Addition to 2,1,3-*Benzothiadiazole* (3).—(i) The foregoing procedure using benzenediazonium-2-carboxylate (10 mmol) and 2,1,3-benzothiadiazole (3) (2.7 g, 20 mmol) followed by chromatographic work-up afforded unchanged (3) (2.3 g, 84%) and the *adduct* (14a) (0.1 g, 5% based on benzyne precursor) as pale yellow needles, m.p. 155—156 °C (from ethanol) (Found: C, 67.7; H, 3.8; N, 13.1. $C_{12}H_{18}N_2S$ requires C, 67.9; H, 3.8; N, 13.2%), $\lambda_{max.}$ 230, 272, and 343 nm (log ε 3.23, 3.29, and 3.28); $\nu_{max.}$ 2 220 (C≡N), 1 622, 1 596, 1 252, 1 160, 997, 815, 775, 763, and 730 cm^{-1}; δ_H 6.04 (1 H, d, H_a), 7.00 (1 H, t, H_c), 7.3—8.0 (3 H, m, H_d H_f, and H_g), and 8.1—8.7 (3 H, m, H_b, H_e, and H_h), J_{ab} 11, $J_{bc} \approx J_{cd} \approx$ 11.5, and $|J_{ac}| \approx J_{ad} \approx$ 1 Hz; *m/e* 213 (60%), 212 (M^+, 75), 186 (100), 140 (15), and 108 (10), *m** 163.4 (212 ⟶ 186).

(ii) Benzyne generation from anthranilic acid and isopentyl nitrite in the presence of a two-fold excess of 2,1,3-benzothiadiazole (3) and work-up as described above gave unchanged (3) (73%) and the adduct (14a) (2.5%).

(ii) Benzyne generation from 1-aminobenzotriazole and lead tetra-acetate in the presence of a four-fold excess of 2,1,3-benzothiadiazole (3) and work-up as described in method (iv) above gave unchanged (3) (81%), biphenylene (59% based on benzyne precursor), m.p. 110—111 °C (from ethanol) (lit.,[27] 110 °C), and the adduct (14a) (10%). In every case the adduct (14a) showed three spots on t.l.c., but the slower-moving components were not isolable in quantity. As with (12a), isomerisation apparently occurs on the alumina plate. The major adduct, purified by recrystallisation, is proved by its ^1H n.m.r. spectrum to be the *cis,cis*-isomer (14a).

Ozonolysis of the Adduct (12a).—(i) Ozone–oxygen was bubbled through a solution of (12a) (2.6 g, 10 mmol) in chloroform (300 ml) at −50 °C until a blue colour persisted. The colour was discharged by further passage of oxygen. The mixture was filtered, and the filtrate was diluted with methanol (50 ml). After 1 h at room temperature the mixture was shaken with water (100 ml) and the organic layer was separated, dried, and evaporated to give a dark red oil. This was chilled and triturated with methanol to give 1,2-benzoselenazole-3-carbaldehyde (13) (42 mg, 2%), m.p. 111—114 °C (from methanol) (lit.,[17] 112—114 °C whereas the isomeric 1,3-benzoselenazole-2-carbaldehyde[18] has m.p. 72 °C) (Found: C, 45.9; H, 2.3; N, 6.6 Calc. for C_8H_5NOSe: C, 45.7; H, 2.4; N, 6.7%), $\nu_{max.}$ 1 696 cm^{-1} (C=O), δ ($CDCl_3$) 10.07 (CHO) (lit.,[17] 10.07). The remainder of the product did not contain unchanged (12a) (by t.l.c.), but chromatography failed to give other components of the mixture pure or crystalline.

(ii) Ozonolysis of (12a) in chloroform on the same scale but at 0—15 °C and an identical work-up yielded *o*-chlorobenzoic acid (0.2 g, 13%), m.p. 137—139 °C (from benzene) (lit.,[28] 139—140 °C), identical (i.r. spectrum and mixed m.p.)

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with an authentic sample. None of the aldehyde (13) was obtained.

Benzyne Addition to 2-Methylbenzotriazole (1; X = NMe). —Benzenediazonium-2-carboxylate [from anthranilic acid (1.37 g, 10 mmol)] decomposed in the presence of 2-methylbenzotriazole [29] (1.3 g, 10 mmol) in refluxing THF as described under method (i). After evaporation of THF the residue was extracted with aqueous hydrochloric acid; the extract was basified and extracted with ether; the ether extract was dried and evaporated to yield phenazine (0.03 g, 2%), m.p. 172—173 °C (from methanol) (lit.,[30] 173—174 °C), identical by i.r. spectrum and mixed m.p. with an authentic sample.[31] Distillation of the acid-insoluble material gave unchanged 2-methylbenzotriazole (0.97 g, 75%), b.p. 102—104 °C at 14 mmHg (lit.,[24] 106—107 °C at 16 mmHg), and left a dark red tarry residue which was a complex mixture (t.l.c.).

We thank Dr. D. Clark for preliminary experiments and Dr. A. J. G. Crawshaw for discussion of n.m.r. spectra.

[7/1852 *Received*, 21*st October*, 1977]

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