Reaction of Benzyne with 1,2,5-Thiadiazoles and 2,1-Benzisothiazoles

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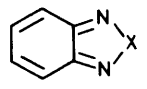
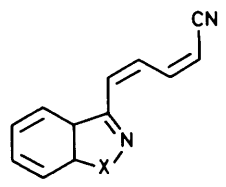
1,2,5-Thiadiazoles react with benzyne to give 1,2-benzisothiazole derivatives. 3,4-Diphenyl-1,2,5-selenadiazole with benzyne likewise affords 3-phenyl-1,2-benzisoselenazole, contrary to a previous report. Some reactions of 3-(8-cyano-1-naphthyl)-1,2-benzisothiazole are described. The reaction of benzyne with 3-amino-2,1-benzisothiazole afforded *N*-phenylated products, including *N*-phenylanthranilonitrile.

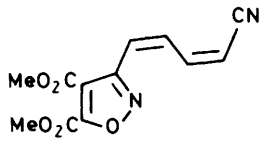
An unusual 1,3-cycloaddition of benzyne across a C=N–Se grouping in 2,1,3-benzoselenadiazole (**1a**) leads to the formation of the rearranged adduct (**2a**).[1] A similar reaction accounts for the formation of small amounts of benzo[*b*]thiophenes from benzyne and thiophenes.[2] An adduct (**3**) structurally analogous to (**2**) is obtained from the benzofuran (**1c**) and dimethyl acetylenedicarboxylate (DMAD) under u.v. irradiation, although the mechanism in this case is entirely different.[3] DMAD adds to (**1a**) to give the quinoxaline (**4e**) and selenium,[1] but such 1,4-cycloaddition to heterocyclic N=C–C=N systems



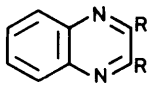
(**1**) **a**; X = Se
b; X = S
c; X = O



(**2**) **a**; X = Se
b; X = S



(**3**)



(**4**) **a**; R = H
b; R = Me
c; R = Cl
d; RR = $[CH_2]_4$
e; R = CO_2Me

is very unusual. The reaction of benzyne with 1,2,5-thiadiazole derivatives has not been reported before, apart from the case of 2,1,3-benzothiadiazole (**1b**) from which the rearranged adduct (**2b**) was obtained in low yield.[1]

Results and Discussion

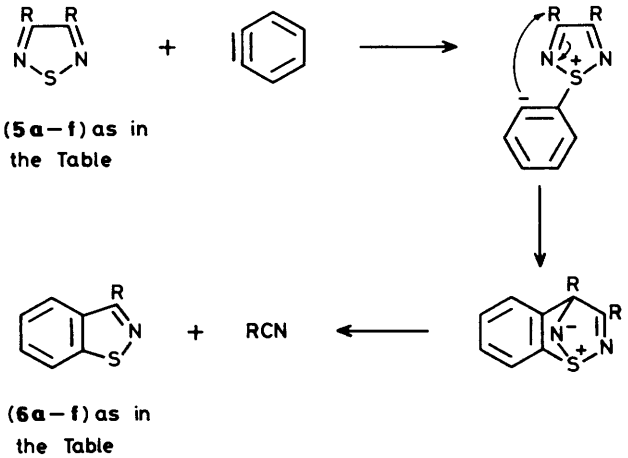
Benzyne generated from benzenediazonium-2-carboxylate reacted with a series of 1,2,5-thiadiazoles (**5a**—**f**) to give in each case the corresponding 1,2-benzisothiazole derivatives (**6a**—**f**) (Table). The identity of compounds (**6a**—**e**) was confirmed by comparison with mass spectral[4] and m.p. data[5–8] available in the literature, and by acidic hydrolysis of compound (**6d**) to give 1,2-benzisothiazol-3-one (**7**).[9] Also the u.v. absorption spectrum of compound (**6b**)[10] is distinctively different from that reported for the isomeric 2-methylbenzothiazole (**8a**).[11]

Table. Reactions of 1,2,5-thia- and selena-diazoles with benzyne

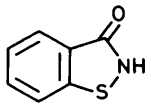
Substrate	Product	% Yield[a]
(**5**)**a**; R = H	(**6**)**a**; R = H[b,c]	25 (74)
b; R = Me	**b**; R = Me[c–f]	31 (62)
c; R = Cl	**c**; R = Cl[c,g]	35[h] (55)
d; R = OEt	**d**; R = OEt[c,i]	75 (83)
e; R = CN	**e**; R = CN[j]	36 (60)
f; RR = $[CH_2]_4$	**f**; R = $[CH_2]_4CN$	30 (53)
(**9**)	(**10a**)	88[h] (95)
(**16a**)	(**17a**)[k,l,m]	90

[a] Yield based on anthranilic acid, except for (**5d**, **e**) where a 2-fold excess of benzyne was used. (Figure in parenthesis is corrected for recovered 1,2,5-thiadiazole). [b] M.p. 35—36 °C [lit.,[5] m.p. 37 °C]. [c] Mass spectrum in agreement with lit. (ref. 4). [d] U.v. spectrum in agreement with lit. (ref. 10). [e] Hydrochloride, m.p. 115—116 °C [lit.,[6] 116 °C]. [f] Also acetonitrile (35%). [g] M.p. 39.5 °C [lit.,[7] 40 °C]. [h] Isolated yield. [i] Hydrolysed with conc. hydrochloric acid at 100 °C to 1,2-benzisothiazol-3-one (**7**), m.p. 158—160 °C [lit.,[8] 157—158 °C]. [j] M.p. 84—86 °C [lit.,[9] 84—86 °C]. [k] M.p. 68—69 °C [lit.,[15] 68—69 °C]. [l] Mass spectrum of compound (**17a**) in agreement with lit. (ref. 16). [m] Also benzonitrile (89%).

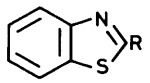
Acetonitrile was readily identified as a complementary product in the case of substrate (**5b**), but in spite of repeated attempts we have been unable to reproduce the formation of 2,3-dimethylquinoxaline (**4b**) and sulphur observed in our first experiments with benzyne and compound (**5b**).[12] Indeed, with authentic samples of the quinoxalines (**4a**—**d**) to hand, none of these was detectable in the product mixtures obtained from benzyne and the 1,2,5-thiadiazoles (**5a**—**c** and **f**). The mechanism which accounts for the formation of these 1,2-benzisothiazoles (**6a**—**f**) is shown in Scheme 1.



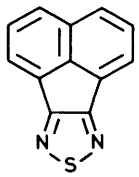
Scheme 1.



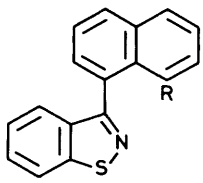
(7)



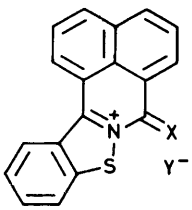
(8) **a**; R = Me
b; R = 1-naphthyl



(9)

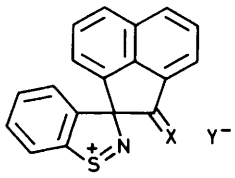


(10) **a**; R = CN
b; R = CO_2Me
c; R = CO_2H
d; R = H

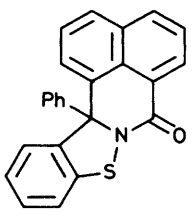


(11) **a**; X = NH
b; X = NH_2^+

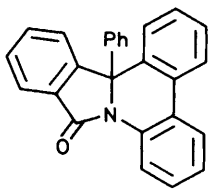
(12) **a**; X = O, Y = ClO_4
b; X = O, Y = Cl
c; X = O, Y = HSO_4



(13)

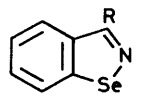


(14)

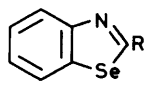


(15)

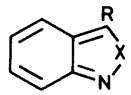
(16) **a**; R = Ph
b; R = Me



(17) **a**; R = Ph
b; R = Me



(18) **a**; R = Ph
b; R = Me



(19) **a**; R = H, X = O
b; R = H, X = S
c; R = NH_2, X = S
d; R = NPh_2, X = S
e; R = Cl, X = S

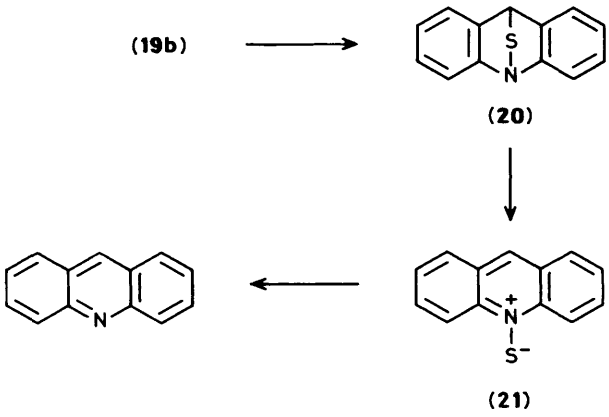
A particularly interesting case is that of the fused 1,2,5-thiadiazole (**9**), which afforded the rearranged benzyne adduct (**10a**) in high yield. This adduct dissolved in conc. perchloric or sulphuric acid to produce an intense red colour which slowly changed to a lighter orange–red on addition of water. We attribute these colours to the initial formation of the pentacyclic cation (**11a**) or its conjugate acid, the dication (**11b**), and then hydrolysis of (**11a**) to give compound (**12**). The alternative structure (**13**) was excluded on the evidence of the weak noise-decoupled ^{13}C n.m.r. spectrum of compound (**10a**) freshly dissolved in $^2H_2SO_4$, which showed resonances for eight non-protonated sp^2 carbon atoms and no signal corresponding to a non-protonated sp^3 carbon upfield of 110 p.p.m.

Treatment of the nitrile (**10a**) with aqueous mineral acids afforded a series of red salts (**12a**—**c**). Repeated recrystallisation of the hydrogen sulphate (**12c**) from methanol or from water gave the colourless methyl ester (**10b**) or the carboxylic acid (**10c**), respectively. Decarboxylation of acid (**10c**) by heating in quinoline with copper bronze gave 3-(1-naphthyl)-1,2-benzisothiazole (**10d**) with m.p. different from that of the isomeric benzothiazole derivative (**8b**).[13] This result provides incidental confirmation of the heterocyclic system in compounds (**10a**—**c**) and hence also that in (**6a**—**f**).

The chloride salt (**12b**) was heated in benzene with aluminium trichloride, whereby we hoped to obtain compound (**14**) on analogy with the formation of compound (**15**) in a related reaction.[14] However, this and other attempts to prepare an uncharged derivative of the pentacyclic system present in the cation (**12**) were unsuccessful.

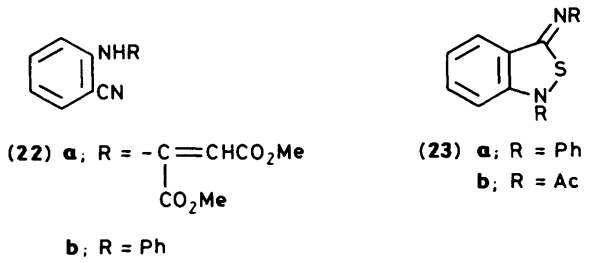
The reaction of benzyne with the 1,2,5-selenadiazoles (**16a** and **b**) was earlier reported to afford the benzoselenazoles (**18a** and **b**) in very low yield,[12] rather than the 1,2-benzisoselenazoles (**17a** and **b**). The formation of the products (**18a** and **b**) was without precedent or satisfactory explanation. Therefore, we reinvestigated the reaction of benzyne with 3,4-diphenyl-1,2,5-selenadiazole (**16a**), from which benzonitrile and 3-phenyl-1,2-benzisoselenazole (**17a**)[15] were obtained (Table). The mass spectrum of compound (**17a**) differs significantly from that of the isomer (**18a**),[16] but examination of the reaction mixture from benzyne and compound (**16a**) by g.c.–m.s. failed to confirm the presence of the benzoselenazole (**18a**) in these later experiments.

Anthranil (**19a**) reacts inefficiently with benzyne (generated by lead tetra-acetate oxidation of 1-aminobenzotriazole) to give acridine.[17] We have found that acridine is also formed in low yield from 2,1-benzisothiazole (**19b**) and benzyne (generated from benzenediazonium-2-carboxylate): the sulphur-bridged cycloadduct (**20**) and/or the *N*-sulphide (**21**) may be intermediates in this reaction (Scheme 2). 2,1-Benzisothiazole (**19b**) reacts in a similar way with acetylenecarboxylate esters to give quinoline esters in low yield, but 3-amino-2,1-benzisothiazole (**19c**) reacts quite differently with DMAD to give the *o*-cyanoanilinofumarate (**22a**).[18] We therefore examined the reaction of benzyne with compound (**19c**), which afforded two products. One of these was *N*-phenylanthranilonitrile (**22b**), presumably formed by a mechanism analogous to that suggested for (**22a**),[18] and identical with a sample prepared by *N*-phenylation of anthranilonitrile with benzyne. The second product was a 1:2 adduct of compound (**19c**) and benzyne, which is most probably the *N*,*N*′-diphenyl derivative (**23a**) analogous to the product (**23b**) of acetylation of compound (**19c**).[19] An alternative structure (**19d**) cannot be definitely excluded, although the u.v. spectrum (see Experimental section) is more consistent with (**23a**), and the formation of compound



Scheme 2.

(**19d**) seems less likely in view of the formation of compound (**22b**) but not an *N,N'*-diphenyl derivative from anthranilonitrile and benzyne. Attempts to confirm the structure by an independent synthesis of 3-diphenylamino-2,1-benzisothiazole (**19d**) foundered on our repeated failure to prepare sufficient quantities of *N,N*-diphenyl-*o*-nitrobenzamide or to achieve any reaction between 3-chloro-2,1-benzisothiazole (**19e**) and diphenylamine under a variety of conditions.



Experimental

U.v. spectra were recorded in solvents stated (Pye Unicam SP8-500). I.r. spectra were recorded for Nujol mulls and calibrated with polystyrene (Unicam SP1025 or Perkin-Elmer 621G or 683). ^{1}H N.m.r. spectra were recorded at 60 (Varian EM360-A) or 90 MHz (JEOL-JNM-FX90Q) and ^{13}C n.m.r. spectra at 22.5 MHz (JEOL-JNM-FX90Q) for solutions in [^{2}H]chloroform with tetramethylsilane as internal standard. Mass spectra were obtained by electron impact at 70 eV (Kratos MS30). Light petroleum refers to the fraction b.p. 40—60 °C. Tetrahydrofuran (THF) was dried before use.

1,2,5-Thiadiazoles (**5a**—**f**)[20–22] and (**9**)[23] and 2,1-benzisothiazoles (**19b** and **c**)[24,25] were prepared according to published procedures. Although 3,4-diphenyl-1,2,5-selenadiazole (**16a**) was obtained as described,[26] the same method proved unsatisfactory for the preparation of the dimethyl analogue (**16b**), so that further work with the latter compound was not possible.

Typical Procedure for Reactions with Benzyne.—Benzenediazonium 2-carboxylate[27] [from anthranilic acid (1.37 g) and pentyl nitrile (1.5 g)] as a slurry in THF was added in portions during 0.5 h to the appropriate 1,2,5-thiadiazole (**5**) (10 mmol) in THF (100 ml), which was heated under reflux during this addition for a further 0.5 h. A sample of this solution was analysed by g.l.c. (Carbowax 20 M) with benzophenone, nitrobenzene, *o*-nitrotoluene, or phenylcyclohexane added as an internal standard to quantify the amounts of both unchanged 1,2,5-thiadiazole and products. The remainder of the reaction mixture was evaporated under reduced pressure, and the residue was chromatographed, fractionally crystallised, or distilled *in vacuo* to give pure samples of the 1,2-benzisothiazoles (**6a**—**f**) and in some cases of recovered (**5**). The products (**6a**—**e**) were identified by comparison of m.p. and mass spectra with those in the literature (see Table), and 5-(1,2-*benzisothiazol*-3-*yl*)-*pentanonitrile* (**6f**), m.p. 63—64 °C (from light petroleum) (Found: C, 66.6; H, 5.5; N, 13.1. $C_{12}H_{12}N_2S$ requires C, 66.6; H, 5.6; N, 13.0%); $\nu_{max.}$ 2 245 (C≡N) and 1 590 cm^{-1} (C=C); δ_H 7.8—8.0 and 7.2—7.6 (each 2 H, m, ArH), 3.13 and 2.39 (each 2 H, t, *J* 7.5 Hz, CH_2), and 1.5—2.2 (4 H, m, CH_2); δ_C 165.1, 152.0, and 134.1 (s, =C), 127.4, 124.3, 122.8, and 119.7 (d, =CH), 119.4 (s, CN), and 30.1, 26.4, 24.7, and 16.6 (t, CH_2); *m/z* 218/216 (M^+, 1/20%), 176 (17), 162 (16), 151/149 (5/100), and 121 (21).

The same reaction procedure using the 1,2,5-thiadiazole (**9**) afforded 8-(1,2-*benzisothiazol*-3-*yl*)*naphthalene*-1-*carbonitrile* (**10a**), m.p. 152—153 °C (Found: C, 75.5; H, 3.5; N, 9.9. $C_{18}H_{10}N_2S$ requires C, 75.5; H, 3.5; N, 9.8%); $\nu_{max.}$ 2 220 (C≡N), 1 595, 1 320, 1 270, 924, 837, 796, 777, 767, 748, and 705 cm^{-1}; δ_H 7.3—8.2 (m, ArH); *m/z* 286 (M^+, 90%), 285 (45), 260 (100), 210 (95), 178 (90), and 105 (95).

Reactions of the Benzyne Adduct (**10a**).—The nitrile (**10a**) dissolved in conc. perchloric or sulphuric acid with an intense red colour ($\lambda_{max.}$ 450 and 529 nm; ε 1 770 and 1 860 m^2 mol^{-1}). On addition of water the spectrum changed over several minutes ($\lambda_{max.}$ 421 and 478 nm; ε 1 310 and 1 610 m^2 mol^{-1}). The weak noise-decoupled ^{13}C n.m.r. spectrum of the red solution of compound (**10a**) freshly dissolved in $^2H_2SO_4$ consisted of the following lines: δ_C 160.1, 157.3, 147.1, 131.8, 127.5, 125.2, 120.0, and 112.7 p.p.m.

The nitrile (**10a**) reacted exothermically with conc. mineral acids, and the salts (**12a**—**c**) were obtained by chilling the resulting red solutions to 0 °C. Thus, compound (**10a**) treated with aqueous perchloric acid (*d* 1.70) or perchloric acid (0.1M) in acetic acid gave the *perchlorate* (**12a**), orange–red crystals, m.p. 215 °C (decomp.) (from aqueous perchloric acid or perchloric acid–acetic acid) (Found: C, 56.3; H, 2.5; N, 3.9. $C_{18}H_{10}ClNO_5S$ requires C, 55.8; H, 2.6; N, 3.6%). Similarly, compound (**10a**) with aqueous hydrochloric acid (6M) gave the chloride (**12b**), bright red crystals, m.p. *ca.* 315 °C (decomp.) and with aqueous sulphuric acid it gave the hydrogen sulphate (**12c**), bright red crystals, m.p. *ca.* 290 °C (decomp.) The salts (**12a**—**c**) had identical u.v. spectra in aqueous acid solution, and the hydrogen sulphate (**12c**), when treated with conc. hydrochloric acid, gave the chloride (**12b**), m.p. undepressed on admixture with the sample obtained directly from compound (**10a**).

Repeated recrystallisation of the hydrogen sulphate (**12c**) from methanol afforded the *methyl ester* (**10b**), needles, m.p. 196—197 °C (Found: C, 71.6; H, 4.2; N, 4.2. $C_{19}H_{13}NO_2S$ requires C, 71.5; H, 4.1; N, 4.4%); $\nu_{max.}$ 1 730 cm^{-1} (C=O); δ_H 7.1—8.1 (10 H, m, ArH) and 3.08 (3 H, s, Me); *m/z* 319 (M^+, 4%), 288 (3), 262 (20), and 261 (100).

Repeated recrystallisation of the hydrogen sulphate (**12c**) from water gave the carboxylic acid (**10c**), m.p. 175—178 °C; $\nu_{max.}$ 2 650br (OH) and 1 690 cm^{-1} (C=O). This acid (**10c**) (200 mg) was dissolved in quinoline (30 ml). Copper bronze powder (3 g) was added; the mixture was heated for 1 h at 150 °C, then cooled and filtered. The filtrate was steam-distilled to remove quinoline, and the tarry residue was extracted with chloroform. The extract was dried ($MgSO_4$) and evaporated under reduced pressure to leave a viscous oil, which was redissolved in the minimum of ether and chromatographed on a column of activated alumina. The eluate obtained with light petroleum–ether (2:1 v/v) afforded 3-(1-*naphthyl*)-1,2-*benzisothiazole* (**10d**) (155 mg, 91%), m.p. 112—113 °C (from methanol) (Found: C, 78.4; H, 4.4; N, 5.45. $C_{17}H_{11}NS$ requires C, 78.2; H, 4.2; N, 5.4%); $\nu_{max.}$ 1 590, 1 320, 1 252, 1 215, 1 012, 938, 808, 782, 771,

and 742 cm^{-1}; *m/z* 263/262/261 (M^+, 3/15/80%), 260 (100), and 259 (16).

Reaction of 2,1-*Benzisothiazoles with Benzyne.*—The crude product mixture obtained from 2,1-benzisothiazole (**19b**) and benzyne by the same general procedure was shown to contain acridine by comparison of g.c. retention time, g.c.–m.s., and fluorescence of the component with appropriate t.l.c. behaviour with those of an authentic sample. The reaction was repeated using 2,1-benzisothiazole (**19b**) (5 mmol) and benzyne (10 mmol) and the formation of acridine (5%) and the presence of unchanged substrate (**19b**) (37%) were quantified by g.c. analysis (10% silicone SE 30 at 180 °C).

The same general procedure using 3-amino-2,1-benzisothiazole (**19c**) (5 mmol) and benzyne (10 mmol) gave, after evaporation of THF, an oil, which was chromatographed on activated alumina. Light petroleum eluted first 1,3-*dihydro*-1-*phenyl*-3-*phenylimino*-2,1-*benzisothiazole* (**23a**) (50 mg, 4%), yellow needles, m.p. 97—99 °C (from light petroleum) (Found: C, 75.5; H, 4.7; N, 9.3. $C_{19}H_{14}N_2S$ requires C, 75.9; H, 4.9; N, 9.2%); $\lambda_{max.}$(EtOH) 388 (ε 1 180 m^2 mol^{-1}), 302sh (1 510), 282 (2 320), 266sh (1 680), and 226 nm (2 780); $\nu_{max.}$ 1 610 (C=N), 1 595, and 1 525 cm^{-1}; δ_H 6.6—8.0 (m, ArH); *m/z* 304/302 (M^+, 5/100%), 269 (35), and 268 (18).

Further elution with light petroleum gave *N*-phenylanthranilonitrile (**22b**) (40 mg, 5%), needles, m.p. 50—52 °C (from light petroleum) (lit.,[28] 47—48 °C), identical in respect of m.p., i.r. spectrum, and t.l.c. behaviour with an authentic sample prepared by reaction of anthranilonitrile with benzyne; no depression of mixed m.p. Elution of the column with light petroleum–ether (1 : 1 v/v) gave benzoic acid (25 mg), which was identified by comparison of its m.p., mass spectrum, and t.l.c. behaviour with those of an authentic sample. Finally, elution with ether returned unchanged compound (**19c**) (0.1 g, 13%).

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