Tetrahedron Vol 39, No. 5, pp. 835 to 837, 1983
Printed in Great Britain

0040-4020/83/050835-03$03.00/0

ADDITION OF BENZYNE TO NAPHTHO[2,3-*c*][1,2,5]SELENADIAZOLE

JOHN M. VERNON, MARTIN R. BRYCE and TREVOR A. DRANSFIELD
Department of Chemistry, University of York, Heslington, York YO1 5DD, England

(*Received in U.K.* 30 *July* 1982)

Abstract—A yellow adduct obtained from benzyne and naphtho[2,3-*c*][1,2,5]selenadiazole is identified as 3-(10-cyano-9-anthryl)-1,2-benzisoselenazole (7). Sequential addition of dimethyl acetylenedicarboxylate and of benzyne to the same fused 1,2,5-selenadiazole affords 3-(4-cyano-2,3-bismethoxycarbonyl-1-naphthyl)-1,2-benzisoselenazole (12).

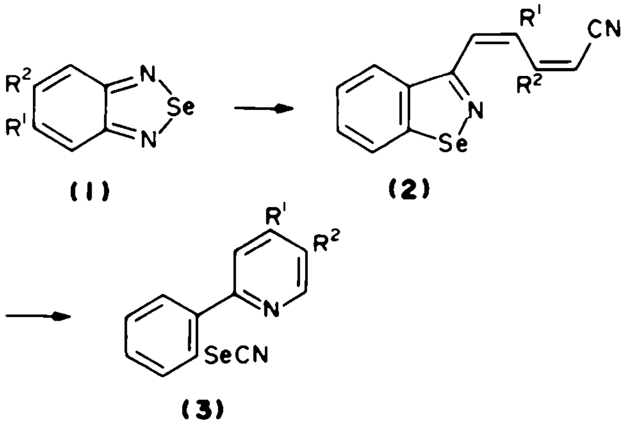
Benzyne adds across a C=N–Se grouping of 2,1,3-benzoselenadiazole (1; $R^1 = R^2 = H$) with rearrangement of the heterocyclic system.[1] The corresponding adducts (2) obtained from benzyne and some substituted 2,1,3-benzoselenadiazoles undergo a further rearrangement to give selenocyanates (3) (Scheme 1).[2] It was therefore of interest to study the reaction of naphtho[2,3-*c*][1,2,5]selenadiazole (4) with benzyne, since the corresponding 1 : 1 adduct (2, R^1, R^2 = CH = CH–CH = CH) containing an *o*-quinodimethane group would be expected to rearrange very readily, if the mechanism suggested for the formation of (3) is correct.

RESULTS AND DISCUSSION

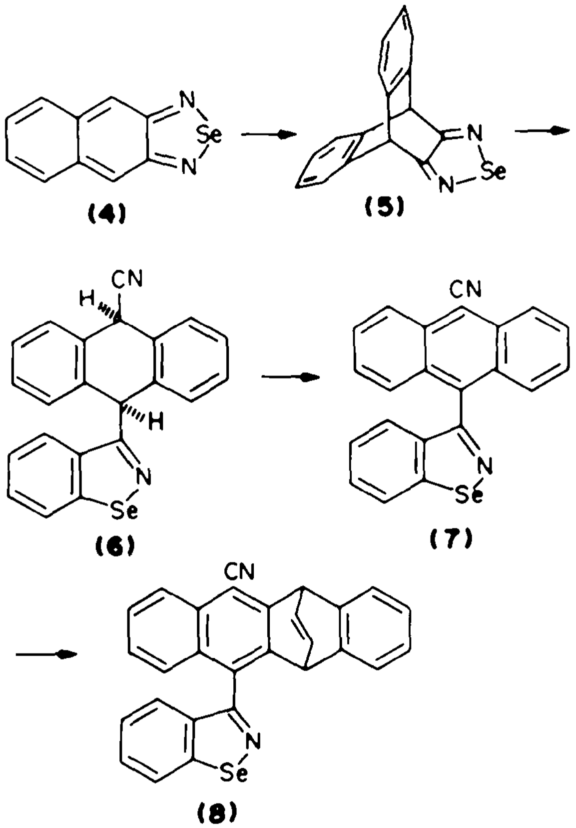
Generation of benzyne (from benzenediazonium 2-carboxylate[3]) in the presence of 4 led to the formation of a yellow adduct with the composition $C_{22}H_{12}N_2Se$, which corresponds to $4 + 2C_6H_4 - H_2$. This material is identified as the anthracene derivative (7) on the basis of IR absorption for a conjugated nitrile group and the very striking similarity of its UV absorption spectrum (Fig. 1) to that of 9-cyano-10-phenylanthracene (9). A by-product, $C_{28}H_{16}N_2Se$, isolated in only trace amount is probably the naphthacene (8), since its nitrile absorption frequency is the same as that of adduct 7. Addition of benzyne across the 9,10-positions of the anthracene moiety of 7 would give rise to a non-conjugated nitrile with a higher frequency IR absorption. Also, the presence of a nitrile group at the 9-position of anthracene is known to divert the addition of benzyne, in part, from the 9,10-positions to the 1,4-positions.[4]

The reaction sequence which best accounts for the formation of the adducts 7 and 8 is outlined in Scheme 2. The initial addition of benzyne to give structure 5 is analogous to the formation of adducts **10a** and **b** from naphtho[2,3-*c*][1,2,5]thiadiazole,[5] which reacts with dienophiles across the middle ring in the same way as anthracene. A second addition of benzyne to the heterocyclic ring in 5 leads to the 9,10-dihydroanthracene (6), which is aromatised possibly by further attack of benzyne. There are several cases known where the 1,4-dihydro aromatic adducts of benzyne and styrene derivatives are aromatised spontaneously under the reaction conditions and the dehydrogenation has been attributed to further attack by benzyne.[6] Among several previously known examples of multiple addition of benzyne, there is none which closely resembles the present case. The first intermediate (5) is interesting as a heterocyclic analogue of triptycene, but unfortunately all attempts to isolate it were unsuccessful.

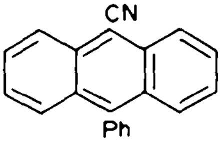
For confirmation of the proposed Scheme, we obtained the adduct 11 from 4 and dimethyl acetylenedicarboxylate, and then the naphthalene derivative (12) by reaction of 11 with benzyne. Both structures 11 and 12 are consistent with appropriate IR and NMR spectroscopic data. Again, the 1,4-dihydro precursor of 12 was not isolated.



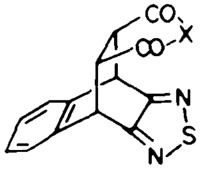
Scheme 1.



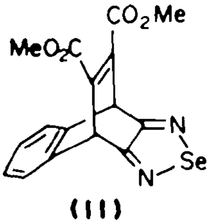
Scheme 2.



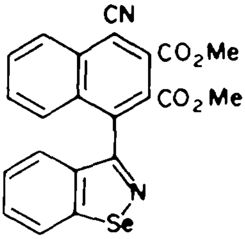
(9)



(10) a; X = O
b; X = NPh



(11)



(12)

EXPERIMENTAL

UV spectra were recorded for CH_2Cl_2 solns using a Pye-Unicam SP800 spectrometer. IR absorptions were recorded for $CHCl_3$ solns on a Perkin-Elmer 683 spectrometer. ^1H and ^{13}C NMR spectra were obtained at 60 MHz (Varian EM360A) and 22.5 MHz (JEOL JNM-FX90Q), respectively, for solns in $CDCl_3$; chemical shifts are quoted in ppm downfield from TMS as internal standard. Mass spectra were obtained by electron impact at 70 eV on a Kratos MS30 spectrometer; only those fragment ions with relative intensity >30% are listed.

Compound 4 was obtained from 2,3-diaminonaphthalene as described,[7] red needles, m.p. 270–275° (dec; lit.[7] ca. 290°); recrystallisation was wasteful because an amorphous pink or colourless solid was deposited from concentrated solns of 4. 9-Cyano-10-phenylanthracene was obtained by heating 9-bromo-10-phenyl-anthracene[8] with Cu(I) cyanide in refluxing dimethyl sulphoxide; yellow crystals, m.p. 201° (lit.[9] 199–200°).

Reaction of 4 with benzyne. Benzenediazonium 2-carboxylate [prepared[1] from anthranilic acid (2.7 g) and pentyl nitrite (4.4 g)] as a slurry in THF was added over 2 hr to a stirred soln of 4

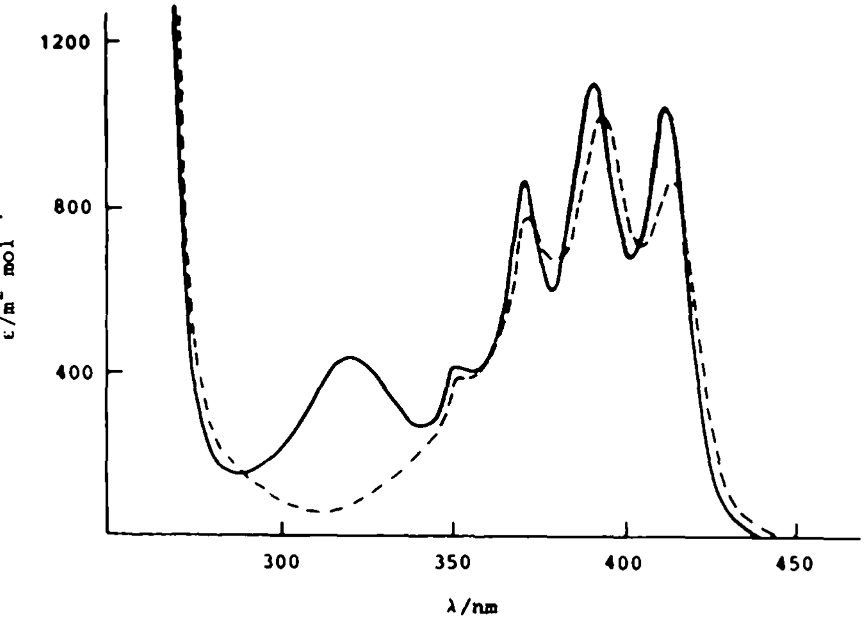


Fig. 1. UV absorption spectra of —— benzyne adduct (7) and ---- 9-cyano-10-phenylanthracene (9).

(1.34 g) in THF (100 ml), which was heated under reflux during this addition and for a further 0.5 hr. The soln was filtered from the amorphous by-product (0.48 g) due to decomposition of 4. The filtrate was evaporated to dryness and the residue chromatographed on alumina, from which CH_2Cl_2 eluted 3-(10-cyano-9-anthryl)-1,2-benzisoselenazole (7; 65 mg, 3%), yellow microcrystals, m.p. 304–305° (from benzene); IR 2 218 cm^{-1} (C≡N); MS *m/e* 386/385/384/383/382/381/380/379 (M^+ overlapping with $M-1$ peaks reflecting Se isotope distribution, 20/37/96/100/55/62/35/20%), 304 (19), and 303 (47). (Found: C, 68.74; H, 3.27; N, 7.35. $C_{22}H_{12}N_2Se$ requires: C, 68.93; H, 3.16; N, 7.31%).

A second yellow fraction eluted from the column with EtOAc afforded 3 - (6,11 - etheno - 6,11 - dihydro - 12 - cyanonaphthacen - 5 - yl) - 1,2 - benzisoselenazole (8; 25 mg), m.p. *ca* 230° (dec); IR 2 217 cm^{-1} (C≡N); MS *m/e* 462/461/460/459/458/457/456 (M^+ peaks reflecting Se isotope distribution, 6/9/25/10/14/8/7%), 380 (59), and 379 (100). (Found: C, 73.11; H, 3.63; N, 6.08. $C_{28}H_{16}N_2Se$ requires: C, 73.20; H, 3.51; N, 6.10%).

UV irradiation through Pyrex of a soln of 7 (10 mg) in CH_2Cl_2 caused a shift in the IR absorption for the nitrile group to 2 257 cm^{-1}, probably as a result of photo-dimerisation across the 9,10-positions of the anthracene ring system (cf 9-cyanoanthracene[10]). Removal of the solvent left a brown gum, from which no pure product was isolated.

Reaction of 4 with dimethyl acetylenedicarboxylate. The acetylene-ester (2.0 g) and 4 (1.7 g) in dry toluene (500 ml) were heated under reflux for 72 hr. The solvent was evaporated and the residue chromatographed on silica gel, from which ether eluted 11, 9,10 - dihydro - 9,10 - (bismethoxycarbonyletheno) - anthracene (0.70 g, 26%), m.p. 203–204° (from MeOH); IR 1 724 (C=O) and 1 634 (C=N) cm^{-1}; ^{1}H NMR 7.0–7.5 (4H, m, ArH), 5.46 (2H, s, tertiary CH), and 3.80 (6H, s, OCH_3); ^{13}C NMR 168.4 and 164.7 (C=O and C=N), 145.6 and 140.3 (quaternary C), 127.3 and 125.4 (ring =CH), 52.8 (OCH_3), and 51.1 (tertiary CH); MS *m/e* 378/377/376/375/374/373/372 (M^+ reflecting Se isotope distribution, 18/17/90/9/45/17/7%), 317 (32), 316 (69), 238 (52), 237 (43), 213 (100), 127 (49), and 59 (61). (Found: C, 51.13; H, 3.25; N, 7.52 $C_{16}H_{12}H_2O_4Se$ requires: C, 51.21; H, 3.22; N, 7.46%).

Reaction of 11 with benzyne. Benzenediazonium 2-carboxylate [prepared[3] from anthranilic acid (0.41 g) and pentyl nitrite (0.64 g)] as a slurry in THF was added over 0.5 hr to a soln of 11 (0.70 g) in THF (80 ml), which was heated under reflux during this addition and for a further 0.5 hr. The solvent was evaporated and the residue chromatographed on silica gel; ether eluted material (0.55 g) which was still a mixture with unsharp m.p. after recrystallisation from MeOH. Rechromatography on alumina, elution with CH_2Cl_2, and fractional crystallisation from MeOH separated 3 - (4 - cyano - 2,3 - bismethoxycarbonyl - 1 - naphthyl) - 1,2 - benzisoselenazole (12; 0.13 g, 16%), m.p. 220–221°; UV 318 nm (1 150 m^2 mol^{-1}); IR 2 271 (C≡N) and 1 736 (C=O) cm^{-1}; ^{1}H NMR 8.40 and 8.00 (each 1H, d, *J* 8 Hz, ArH), 7.1–7.9 (6H, m, ArH), and 4.01 and 3.42 (each 3H, s, OCH_3); MS *m/e* 452/451/450/449/448/447/446/445 (M^+ overlapping with $M-1$ peaks reflecting Se isotope distribution, 21/30/100/52/53/40/26/8%) and fragment ion multiplets dominated by the following peaks for ^{80}Se: 419 (M − OMe]$^+$ (38), 391 [M − CO_2Me]$^+$ (34), and 332 [M − CO_2Me − CO_2Me]$^+$ (33). (Found: C, 58.92; H, 3.10; N, 6.26. $C_{22}H_{14}N_2O_4Se$ requires: C, 58.81; H, 3.14; N, 6.24%). Further quantities of 12 in other fractions were incompletely separated from unreacted 11.

REFERENCES

[1] C. D. Campbell, C. W. Rees, M. R. Bryce, M. D. Cooke, P. Hanson and J. M. Vernon, *J. Chem. Soc. Perkin Trans.* 1, 1006 (1978).

[2] M. R. Bryce, C. D. Reynolds, P. Hanson and J. M. Vernon, *Ibid., Perkin Trans.* 1, 607 (1981).

[3] F. M. Logullo, A. H. Seitz and L. Friedman, *Org. Synth. Coll.* 5, 54 (1973).

[4] B. H. Klanderman, *J. Am. Chem. Soc.* 87, 4649 (1965).

[5] M. P. Cava and R. H. Schlessinger, *Tetrahedron Letters* 3815 (1964).

[6] W. Davies and J. R. Wilmshurst, *J. Chem. Soc.* 4079 (1961); S. F. Dyke, A. R. Marshall and J. P. Watson, *Tetrahedron* 22, 2515 (1966); E. Wolthuis and W. Cady, *Angew. Chem.* Int. Ed. Engl. 6, 555 (1967).

[7] C. A. Parker and L. G. Harvey, *Analyst* 87, 558 (1962).

[8] J. W. Cook, *J. Chem. Soc.* 2160 (1926); C. Dufraisse, L. Velluz and L. Velluz, *Bull. Soc. Chim. Fr.* 4, 1260 (1937).

[9] C. Dufraisse and P. Mathieu, *Ibid.* 302 (1947).

[10] R. Calas, R. Lalande and P. Mauret, *Ibid.* 148 (1960); H. Bouas-Laurent and R. Lapouyarde, *Chem. Commun.* 817 (1969).