Mechanism of the Photoreaction between 1,4-Dicyanonaphthalene and Benzylic Donors

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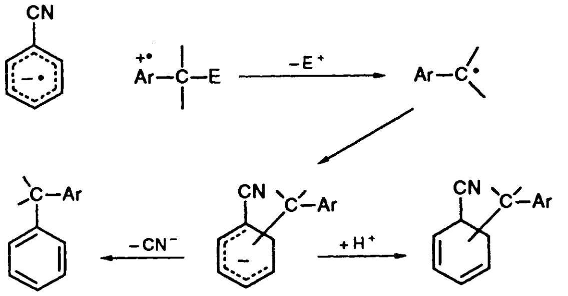
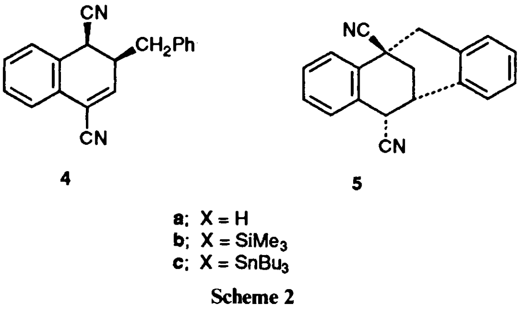
The reaction of 1,4-dicyanonaphthalene (DCN) with ethylbenzene, propylbenzene, and α-methylbenzyltrimethylsilane has been investigated and compared with previous results obtained using other benzylic donors. The relative yield of the different types of reaction observed, (*a*) substitution of a cyano group to yield naphthalenes **2**, (*b*) addition to yield the dihydronaphthalenes **3** and **4**, and (*c*) addition with cyclization to yield the tetracyclic derivatives **5** as well as the diastereoisomeric distribution within each type of product, show that these reactions occur by different paths, all initiated by electron transfer, involving respectively cleavage of the free radical cation [for case (*a*)], detachment of a proton or a silyl cation and (probably concerted) addition to DCN$^{\cdot -}$ [for case (*b*)], and proton transfer within the initial radical ion pair [for case (*c*)].

Alkylation, and in particular benzylation, of aromatic nitriles can be effected by irradiation in the presence of appropriate donors.[1-6] Electron transfer to the excited nitrile generates the radical cation and this cleaves by loss of a proton or another electrofugal group, to yield a benzyl radical, which then adds to the radical anion. In the final step the anion rearomatizes (the predominant reaction with benzenecarbonitriles) or is protonated to give a dihydroaromatic molecule (predominant with naphthalenes and other condensed aromatics, since a partial loss of aromaticity is acceptable, Scheme 1). With 1,4-dicyanonaphthalene (DCN) there is a wider product distribution[7-11] (Scheme 2) and several attempts have been made to explain this peculiar reactivity and its relevance to the general mechanism. Although much is now known, it cannot be said that the problem is fully settled, *e.g.* with regard to the crucial question of whether free radical ions or ion pairs are involved.



Scheme 1

Herein we report some further effort towards this aim using donors of general formula PhCHRX (R = H, Me, Et; X = H, SiMe$_3$).



Scheme 2

Results and Discussion

As previously reported,[7-10] toluene (**1a**) yields products **2a**–**5a** (Scheme 2), with **3a** in trace amounts and the tetracyclic derivative **5a** as the main product (Table 1). With benzyltrimethylsilane (**1b**) **3a** and **4a** are obtained in high yield, and the stannane **1c** yields **2a**, **3a** and **4a** (all reactions are performed in acetonitrile).

With ethylbenzene (**1d**), besides the product resulting from substitution of a cyano group (**2d**), five further derivatives were obtained (Scheme 3).

Firstly a diastereoisomeric pair of 1-alkyl-1,4-dicyano-1,2-dihydronaphthalenes (**3d** and **3′d**), where ^{1}H NMR spectra exhibit different methylene group signals. In a related case [the 1-(α-methoxybenzyl) derivative][11] we have attributed structure **3** to the isomer in which the resonances of these two protons are very close to one another and structure **3′** to the isomer where they are more widely spaced, on the basis of MM2 calculations; since there is a similar spectral difference here (see Experimental section), a tentative assignment might be made in the same way.

A second diastereoisomeric pair of 2-alkyl-1,4-dicyano-1,2-dihydronaphthalene (**4d** and **4′d**) was obtained. Here the coupling constants $J_{1,2}$ and $J_{2,3}$ show that the ring substituents in positions 1 and 2 are in a *cis* arrangement, and the diastereoisomerism results from the configuration of the α-benzyl centre; since the spectra are almost superimposable, we have no evidence for a complete assignment.

Finally a single tetracyclic derivative (formula **5d** or **5′d**) was obtained. Accurate NMR and HPLC examination of the fractions obtained showed no evidence for the other isomer.

With trimethyl(α-methylbenzyl)silane (**1e**) all the above products, except the tetracyclic derivative **5** were obtained, but in different yields (Table 1).†

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† Isolated yields are reported in Table 1. HPLC analysis showed that no other adduct was present in significant amounts, and gave a product distribution similar to the isolated one. The diasteroisomeric ratio **3**/**3′**, **4**/**4′** was ill obtained by this method. However, examination of the chromatographic mixtures containing pairs of isomers confirmed ratios **3**/**3′d** *ca.* 2 from **1d** and *ca.* 1 from **1e**, and **4d**/**4′d** *ca.* 0.7 from both sources.

Table 1 Products from the irradiation of DCN in the presence of benzylic donors in acetonitrile

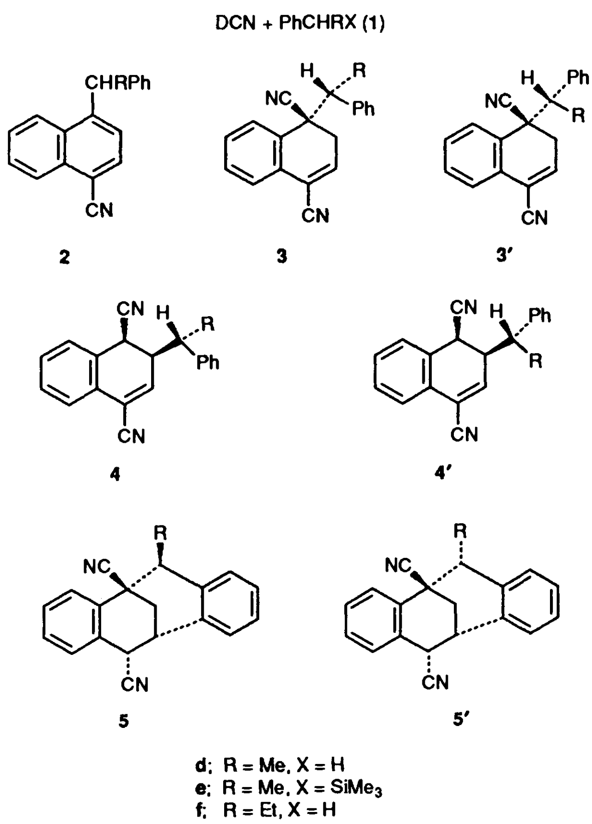
Donor	Products (% yield)
1a[a]	**2a** (12), **3a** (2), **4a** (8), **5a** (23)
1b[b]	**3a** (30), **4a** (70)
1c[b]	**2a** (39), **4a** (20), **5a** (30)
1d	**2d** (23), **3d** (11), **3′d** (5), **4d** (20), **4′d** (14), **5d** (17)
1e	**2d** (10), **3d** (19), **3′d** (17), **4a** (20), **4′d** (15)

[a] See ref. 7. [b] See ref. 10.

Table 2 Steady state parameters in acetonitrile

Donor	K_{sv}/dm^3 mol^{-1}	k_q/dm^3 mol^{-1} s^{-1} [c]	φ (0.02 mol dm^{-3})
1a[a]	19	1.9×10^9	0.02
1b[b]	115	11.5×10^9	0.25
1d	20	2.0×10^9	0.016
1f	17	1.7×10^9	0.008

[a] See ref. 8. [b] See ref. 10. [c] Rate constants for the quenching of the DCN singlet state, calculated from the known τ_s of 10.0 ns, see ref. 12.



Scheme 3

In an effort to establish the effect of the length of the chain on the reaction, propylbenzene (**1f**) was examined. However, the reaction was much slower and we were unable to obtain a satisfactory chromatographic separation (in part this is due to the long irradiation time required, and thus to the occurrence of some secondary photodecomposition). However, spectroscopic examination of the fractions obtained showed, with a fair degree of certainty, that all expected products (**2**, **3**, **3′**, **4**, **4′**, **5**, **5′f**), were present (see the Experimental section).

Finally, L-menthyl *p*-ethylphenylacetate was tested as donor, with a view to checking the possible influence of a chiral centre (admittedly, not very near to the reaction site). However, the reaction appeared to be too slow to yield meaningful results.

Stern–Volmer constants for fluorescence quenching as well as quantum yields for photoreaction of DCN at 0.02 mol dm^{-3} donor concentration are reported in Table 2.

The above data show that these reactions involve electron transfer quenching of DCN*[1] by the donor ($\Delta G_{et} < 0$ in all cases) and cleavage of the radical cation to form benzyl radicals. The question is, how does this latter step take place? Thermochemical cycles allow the calculation of the bond dissociation enthalpy for the radical cations involved on the basis of the known oxidation potential of the neutral donor and of the reduction potential of the cation formed (see refs. 13, 14 for similar applications). It turns out that deprotonation is a facile process (*e.g.* the calculated[14] ΔH for reaction (1) is −17 kcal mol^{-1}),† while departure of a silyl cation encounters a sizeable barrier [ΔH for reaction (2) is in the range 32–42 kcal mol^{-1} ‡; other authors[6] have considered 30 kcal mol^{-1}).

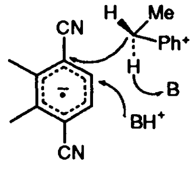
$$PhCH_3^{\cdot+} \longrightarrow PhCH_2^{\cdot} + H^+ \tag{1}$$

$$PhCH_2SiMe_3^{\cdot+} \longrightarrow PhCH_2^{\cdot} + SiMe_3^{+} \tag{2}$$

Using these values for predicting the preferred path of reaction is subject to some limitations (some of the data used are in the gas phase; it is assumed that the entropy term does not unbalance the conclusions, since charged species, the solvation of which makes the largest contribution to this term, are present on both sides of the equation), but nevertheless eqn. (1) should be an efficient process, provided that there is a suitable accepting base, while it is less likely that the unimolecular cleavage represented by eqn. (2) competes favourably with back electron transfer. Since the radical anion is a poor base proton transfer is not very fast, and quantum yields with hydrocarbons as donors are rather low; on the other hand, the silanes do undergo desilylation rather than deprotonation, and this suggests that the process is more complicated than represented in eqn. (2).

The products obtained are grouped in Table 3 according to the reaction type (substitution: products **2**; addition: products **3** and **4**; addition with cyclization: products **5**). The preference for one or the other of these groups, and the stereochemistry of product formation within each of them, helps in elaborating the mechanism as proposed on the basis of previous findings.

Addition takes place by detachment of a proton or another cation from the radical cation, addition of the benzyl radical to $DCN^{\cdot-}$ and stereoselective protonation of the anion thus formed. Notice that with ethylbenzene one of the 1-alkyl diastereoisomers (**3d** if our assignment is correct) is obtained in a larger proportion. Let us make the hypothesis that the radical cation fragments when still complexed to the radical anion. The C–H σ bond to be cleaved must be perpendicular to the benzene



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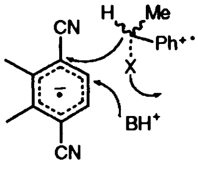

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† 1 cal = 4.184 J.

‡ Estimated from the bond dissociation energy of the silane, 75 kcal mol^{-1} (refs, 6, 15) its ionisation potential, 8.35 eV (ref. 16) and the E_i of the radical, as estimated from the appearance potential of the ion, 6.93 to 6.61 eV (ref. 17).

Table 3 Type of photoprocess observed[a]

	1a	**1b**	**1c**	**1d**	**1e**
Substitution	27		44	26	12
Addition	22	100	56	19	88
Addition with cyclization	51			56	

[a] % Yield calculated on the total amount of isolated photoproducts.

ring and conformation **6** predominates (in the alternative conformation, with phenyl and methyl exchanged, steric hindrance is larger). As for the silanes, in view of the above thermodynamic considerations, rather than an unimolecular process, cleavage of donors **1b** and **1e** may be conceived as a concerted process leading to the anion which is directly reprotonated. From the stereochemical point of view the requirement that the bulky $SiMe_3$ group is held perpendicular makes the position of the methyl group unimportant (see formula **7**), and products **3d** and **3′d** are in this case obtained in equal amounts.

The other addition process (attack at position 2) leads to product **4**. In this case addition involves an unsubstituted position, steric hindrance is less important, and products **4d** and **4′d** are obtained in the same amounts from both ethylbenzene and the silane **1e**.

Substitution involves initial separation of the ions and cleavage of the free radical cation followed by attack of the benzyl radical onto $DCN^{\bullet -}$. The faster reaction of the solvated anion thus formed is apparently cyanide loss rather than protonation. Thus, substitution is not observed with silane **1b** because the unimolecular cleavage according to eqn. (2) is too slow, and becomes more important when the bond to be broken is weakened (**1c** > **1e** > **1b**).

Additive cyclization involves proton transfer within a tight ion pair. It does not take place with the silanes and stannanes (where there is a more convenient electrofugal group, and attainment of the correct conformation for proton transfer is difficult). There is no reason why **5d** and **5′d** should appreciably differ in energy, and thus the fact that only one of them is formed from **1d** emphasizes the stringent steric requirements in the reactive complex. Furthermore mere homologation to **1f** makes attainment of the correct conformation much more difficult, causing a large drop in both reaction rate (as deduced from the quantum yield, which is reduced much more than the quenching constant) and stereoselectivity (both isomeric **5** formed with **1f**, only one with **1d**).

Thus, in accordance with evidence obtained with other donors, in particular the reaction between DCN and the cymenes,[18] it appears that after electron transfer, radical cation cleavage and formation of the new carbon–carbon bond(s) take place according to different paths, where the key intermediate ranges from a more or less tight ion-pair to the free, solvent-stabilized ions.

This work concludes our study, which has been in progress for several years, of the photochemical reaction between cyanonaphthalenes and alkylbenzenes and related substrates. During this time the chemistry of photochemically generated radical ions has grown into a popular field of research. In the present reaction the properties of the radical ion pair, the limit at high charge separation of the classic exciplex, are more important than those of the free radical ions, and this is probably not an isolated case.

Experimental

Materials.—DCN and the benzyl derivatives were prepared according to literature procedures. Trimethyl(α-methylbenzyl)silane (**1e**) was prepared by reacting chlorotrimethylsilane with the anion prepared by treating α-methylbenzyl methyl ether with potassium in heptane.

Physical Data.—UV spectra were recorded with a Cary 19 spectrophotometer, IR spectra for KBr pellets by means of a Perkin-Elmer 197 Spectrophotometer, ^1H NMR spectra in $CDCl_3$ by means of a Bruker 300 instrument with tetramethylsilane as internal standard (*J* values in Hz), mass spectra by means of a Du Pont DU2 instrument, and elemental analyses by means of a Carlo Erba 1106 analyser. The reactions were followed by HPLC using a Waters 501 instrument equipped with an UV detector 490.

Photochemical Reaction between 1,4-*Dicyanonaphthalene* (*DCN*) *and Ethylbenzene* **1d**.—A solution of DCN (200 mg) and ethylbenzene (2 cm^3) in acetonitrile (80 cm^3) was brought to boil and cooled under argon. The cooled solution was irradiated by means of a Helios Italquarz 125 W medium pressure mercury arc until DCN was largely consumed (2 h). Evaporation of the solution and chromatography of the residue on a column of silica gel Merck 60 HR, eluting with cyclohexane and then cyclohexane–ethyl acetate (8:2) gave unchanged DCN (20 mg) and the following products: 4-Cyano-1-(α-methylbenzyl)naphthalene (**2d**, 59 mg, 23%), colourless crystals, m.p. 55 °C (from ethanol) (Found: C, 88.7; H, 5.9; N, 5.4. Calc. for $C_{19}H_{15}N$: C, 88.7; H, 5.9; N, 5.4%); δ_H 1.8 (d, 3 H, *J* 7), 4.95 (q, 1 H), 7.5 (d, 1 H, *J* 8, 2-H), 7.9 (d, 1 H, 3-H) and 7.3–8.3 (m, 9 H, aromatic). 1,4-Dicyano-1-(α-methylbenzyl)napthalene (**3d**, 31 mg, 11%), colourless crystals, m.p. 204–205 °C (from ethanol) (Found: C, 84.4; H, 5.7; N, 9.8. Calc. for $C_{20}H_{16}N_2$: C, 84.5; H, 5.7; N, 9.9%); δ_H[2.85 (dd, 1 H, *J* 19 and 6) and 2.55 (dd, 1 H, *J* 19 and 3) CH_2 in position 2], 6.7 (dd, 1 H, *J* 6 and 3, 3-H), 1.5 (d, 3 H, *J* 7, Me), 3.05 (q, 1 H, α-CH). 1,4-Dicyano-1-(α-methylbenzyl)naphthalene (**3′d**, 14 mg, 5%) obtained from the mother liquid from the recrystallization of the previous isomer, colourless crystals, m.p. 188–192 °C (from ethanol) (Found: C, 84.7; H, 5.8; N, 9.5%); δ_H[3.12 (dd, 1 H, *J* 19 and 6) and 3.0 (dd, 1 H, *J* 19 and 4) CH_2 in position 2], 6.6 (dd, 1 H, *J* 4 and 6, 3-H), 1.3 (d, 3 H, *J* 7, Me), 3.0 (q, 1 H, α-CH), 7.1–7.5 (m, 9 H, aromatic). 1,4-Dicyano-2-(α-methylbenzyl)naphthalene (**4d** or **4′d**, 57 mg, 20%), colourless crystals, m.p. 161–165 °C (from ethanol) (Found: C, 84.6; H, 5.8; N, 9.7%); δ_H 3.55 (d, 1 H, *J* 5.5, 1-H), 2.95 (ddd, 1 H, 2-H), 6.9 (d, 1 H, *J* 2.5, 3-H), 3.15 (dq, 1 H, α-CH), 1.55 (d, 3 H, *J* 6.5, Me), 7.1–7.5 (m, 9 H, aromatic). 1,4-Dicyano-2-(α-methylbenzyl)naphthalene (the other isomer, 40 mg, 14%), obtained from the mother liquor from the recrystallization of the previous isomer, colourless crystals m.p. 139–140 °C (from ethanol) (Found: C, 84.2; H, 5.9; N, 9.6%); δ_H 4.2 (d, 1 H, *J* 5.5, 1-H), 3.05 (ddd, 2-H), 6.45 (d, 1 H, *J* 2.5, 3-H), 3.2 (dq, 1 H, α-CH), 1.45 (d, 3 H, *J* 6.5, Me), 7.1–7.5 (m, 9 H, aromatics). 5,12-Dicyano-6-methyl-5,11-methano-5,6,11,12-tetrahydrodibenzo[*a*,*e*]cyclooctene (**5d** or **5′d**, 48 mg, 17%), colourless crystals, m.p. 225–230 °C (from ethanol) (Found: C, 84.5; H, 5.7; N, 9.8); δ_H 1.5 (d, 3 H, *J* 7, Me), 3.6 (q, 1 H, 6-H), [2.7 (dd, 1 H, *J* 2.5 and 13) and 2.8 (dd, *J* 4.5 and 13), methano bridge], 3.65 (ddd, 1 H, 1-H), 4.55 (d, 1 H, *J* 4.5, 12-H), 7.2–7.6 (m, 8 H, aromatic).

Photochemical Reaction between DCN and Trimethyl-α-methylbenzylsilane **1e**.—The reaction between DCN and **1e** (2 cm^3) was carried out (irradiation time, 45 min) and worked up as above. The yield of the products are reported in Table 1.

Photochemical Reaction between DCN and Propylbenzene **1f**.—The reaction between DCN and **1f** (2 cm^3) was carried out (irradiation time 48 h) and worked up as above. Despite repeated chromatography of the fractions from the first separation, the products were not obtained in the pure state.

However, the two isomers **3f** and **3′f** were present (δ_H the ABX systems at 2.5, 2.75 and 6.62 and at 3.1, 3.25 and 6.65 respectively) and so were the two isomers **5f** and **5′f** (δ_H 2.62, 2.75 and 3.67 for the ABX system, 4.55 for 12-H and 2.4, 2.85, 3.45 for the ABX system and 4.5 for 12-H) as well as **4f–4′f** (indistinguishable by NMR spectroscopy), **2f** and some *meso*-3,4-diphenylhexane.

Steady State Measurements.—Fluorescence measurements were made on degassed 10^{-5} mol dm^{-3} solutions of DCN by means of an Aminco-Bowman MPF spectrofluorimeter. Reaction quantum yields were measured on degassed 10^{-4} mol dm^{-3} solutions of DCN in 1 cm optical path cuvettes on an optical bench. Light from an Osram 200 W high-pressure mercury arc was focussed and monochromatized by means of an interference filter. Light intensity was measured by ferrioxalate actinometry. An absorbed-flux of *ca.* 10^{-7} einstein min^{-1} cm^{-2} was obtained.

Acknowledgements

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