

## Set Photochemical Reactions between 1,4-Naphthalenedicarbonitrile and Benzylic Donors. Medium Effects

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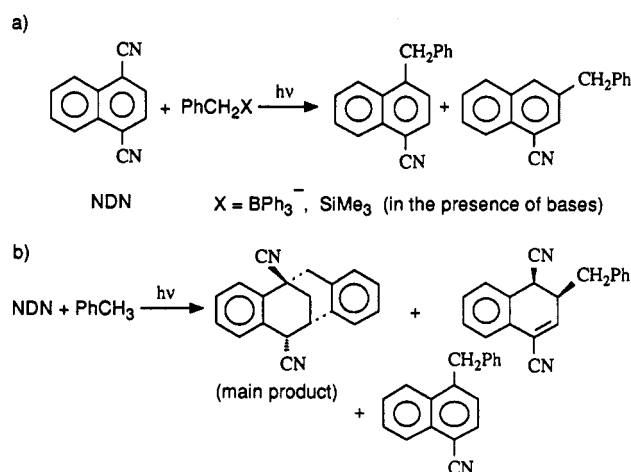
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The electron transfer induced photochemical reactions of 1,4-naphthalenedicarbonitrile (NDN) with toluene (1a), diphenylmethane (1b), *p*-methoxytoluene (1c), and benzyltrimethylsilane (1d) in MeOH-MeCN and 0.1 M KOH-MeOH-MeCN were examined. The results were compared with those of reactions occurring in neat MeCN. Under the former conditions, the cation radical derived from 1a undergoes deprotonation after diffusion from (rather than within) the geminate ion pair (as in MeCN). The formed benzyl radical abstracts a hydrogen from MeOH leading to hydroxymethylation of NDN competitively with its benzylation. Under basic conditions MeO<sup>-</sup> adds to 1a<sup>•+</sup> yielding 1c. The reaction of 1b in MeOH-MeCN and 0.1 M KOH-MeOH-MeCN is similar to that of 1a. However, in the reaction of 1c under these conditions, the arene cation radical undergoes deprotonation out of cage. Finally, desilylation of the cation radical from 1d is a fast process occurring from the geminate pair in all the media explored.

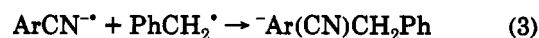
Alkylation of aromatics via photoinduced electron transfer (PET) has received considerable recent attention.<sup>1-7</sup> These reactions are promoted by electron transfer from donors (e.g. a benzylic derivative) to excited aromatics (often an arenecarbonitrile). Fragmentation of radical cation intermediates occurs to form neutral radicals which add to the radical anion of the arene acceptor to generate the aromatic substitution products (eqs 1-4).

An example of these processes is the benzylation of 1,4-naphthalenedicarbonitrile (NDN) with tetramethylammonium benzyltriphenylborate<sup>6b</sup> or benzylsilane in the

Scheme 1



presence of bases<sup>5c</sup> leading to 3- and 4-benzyl-1,4-naphthalene-1-carbonitrile (Scheme 1a).



The detailed mechanism of the PET alkylation is not yet completely understood in the sense that the timing and precise nature of the steps, represented in possibly an over-simplified way in eqs 1-4, have not been fully clarified. Important questions that remain unanswered include (1) does the radical cation cleave through the assistance of a nucleophile, (2) does the radical anion itself (though this

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is a poor base in the case of arenecarbonitriles) accept the cation  $X^+$ , at least when this is a proton, and (3) is the C–C bond formed during reencounter of the radical and the radical anion (the last species is quite stable with arenecarbonitriles and may accumulate), or does the entire sequence occur without separation directly from the initially formed radical ion pair? Although we make specific reference here to the PET alkylation of aromatics, these questions are more generally relevant to all reactions involving the fragmentation of PET-generated radical cations.<sup>8</sup>

These questions have been probed by use of several different methods. One approach has involved measurement by flash photolysis of the yield of free radical cations and a direct determination of the rate of their reaction.<sup>7a,b,c</sup> It is not always trivial to establish the relation between the observed transient decay and the actual chemical reaction, and in addition, flash spectroscopic methods cannot be used to probe other steps in those complex sequences leading to the final product and where non-absorbing intermediates are involved. Therefore, although having their own limitations, product studies often complement more physically oriented studies in defining the precise mechanisms for PET-induced reactions.

With these ideas in mind we have reexplored the PET reaction between NDN and alkylbenzenes. The previously studied reaction of NDN with toluene (see Scheme 1b) represents one mechanistic extreme for these processes, in the sense that proton transfer occurs within the initially formed radical ion pair and is followed by direct addition to give a tetracyclic derivative as the main product.<sup>3</sup> This type of reaction occurs with several alkylbenzenes, but it is not general. Some benzylic derivatives yield benzylated dihydronaphthalenedinitriles or rearomatized naphthalenedinitriles rather than tetracyclic derivatives.<sup>3,9</sup> We reasoned that changing the nucleophilicity of the medium may result in a gradual change of the product distribution (as observed in other reactions involving radical cation fragmentation).<sup>10</sup> This effect, coupled to the above-mentioned dependence of the reaction on the structure of the donor, would lead to useful mechanistic information about the cyanoarene–benzylic donor PET reactions.

## Results

Toluene (1a), diphenylmethane (1b), 4-methoxytoluene (1c), and benzyltrimethylsilane (1d) were chosen as benzylic donors for the present study. The products obtained by irradiation of NDN in the presence of these donors in acetonitrile (conditions  $\alpha$ ), as determined in previous work,<sup>3a,d,g</sup> are shown in Scheme 2 and the yields are given in Table 1. We have now examined the photochemical reaction of NDN and these same donors

Scheme 2

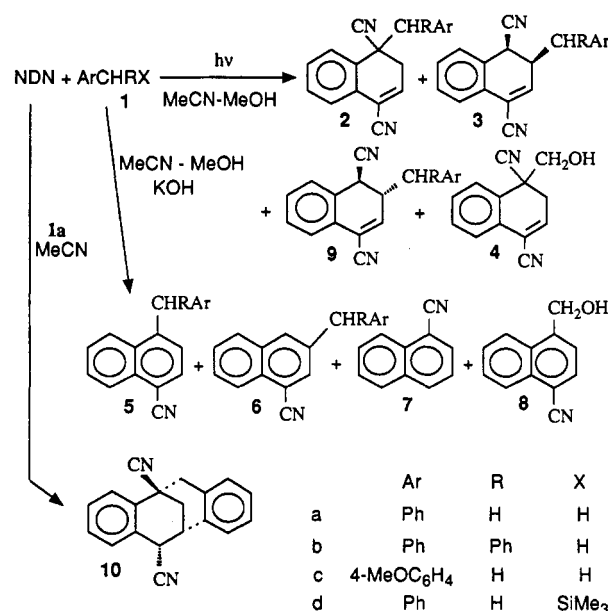


Table 1. Products from the Preparative Irradiation of NDN in the Presence of Benzylic Donors

donors	conditions <sup>a</sup>	photoproducts (% yield)
1a	$\alpha^{b,c}$	2a (tr), 3a (8), 5a (12), 10 (35)
	$\beta^c$	2a (6), 3a (tr), 4 (30)
	$\gamma^d$	5a (tr), 6a (tr), 7 (8), 8 (15)
1b	$\alpha^{e,f}$	3b (45), 9b (11)
	$\beta^g$	2b (15), 3b (5), 4 (25), 9b (2)
	$\gamma^g$	7 (15), 8 (10)
1c	$\alpha^{h,i}$	2c (17), 3c (26), 5c (19), 9c (10)
	$\beta$	2c (58), 3c (8), 5c (23), 9c (2)
	$\gamma$	5c (13), 6c (2), 7 (40)
1d	$\alpha^e$	2a (70), 3a (30)
	$\beta$	2a (72), 3a (25)
	$\gamma$	5a (65), 6a (18)

<sup>a</sup> Condition  $\alpha$ : by irradiation in MeCN;  $\beta$ : in MeCN–MeOH 1:1;  $\gamma$ : in 0.1 M KOH in MeCN–MeOH 1:1. <sup>b</sup> From ref 3a. <sup>c</sup> 15 mg of bibenzyl is also obtained (see Experimental Section). <sup>d</sup> Bibenzyl (10 mg) and *p*-methoxytoluene (30 mg) are also obtained. <sup>e</sup> From ref 3d. <sup>f</sup> 1,1,2,2-Tetraphenylethane (20 mg) also obtained. <sup>g</sup> 1,1,2,2-Tetraphenylethane is also obtained (15 mg). <sup>h</sup> From ref 3g. <sup>i</sup> 1,2-Bis(4-methoxyphenyl)ethane (20 mg) is also obtained.

in an 1:1 acetonitrile–methanol mixed solvent system (condition  $\beta$ ) and in the presence of bases (condition  $\gamma$ ).

Irradiation of NDN in the presence of 1a in 1:1 MeCN–MeOH gives none of the tetracyclic product observed for the reaction in pure MeCN (Scheme 1b). The main toluene adduct formed under these conditions is 1-benzyl-1,2-dihydro-1,4-naphthalenedicarbonitrile (2a) (a trace product for the reaction in neat acetonitrile). A lesser amount of the corresponding *cis*-2-benzyl derivative 3a is also produced. However, the main product from the photo-reaction of NDN with 1a is the alcohol adduct 4.

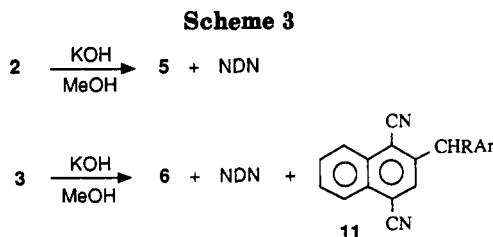
When NDN and 1a are irradiated in MeCN–MeOH containing 0.1 M KOH, the solution becomes dark and the material balance is poor. The product distribution changes again. Thus, 4-benzyl-1-naphthalenedicarbonitrile (5a), its 3-benzyl isomer 6a, and 1-naphthalenedicarbonitrile (7) are formed only in traces, along with the (hydroxy-methyl)naphthalene 8 as the (relatively) major product. Finally, for photoreactions conducted under  $\alpha$  and  $\beta$  conditions small amounts of bibenzyl are formed, whereas under the  $\gamma$  condition *p*-methoxytoluene is a major byproduct.

The photochemical reaction of NDN and diphenyl-

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methane (1b) under condition  $\beta$  gave the 1-benzhydryl-1,2-dihydronaphthalene (2b), a product not formed in neat MeCN, as well as the 2-substituted derivatives (both stereoisomers, 3b and 9b, as in MeCN). As in the case of 1b, the major product formed is the alcohol 4. Under the  $\gamma$  conditions the balance is again poor, and no appreciable amount of benzylated products are obtained, but instead, the naphthalenemethanol 8 and the mononitrile 7 are formed. Under all the conditions used, 1,1,2,2-tetraphenylethane is formed in low yields.

The reaction of NDN and *p*-methoxytoluene (1c) in MeCN–MeOH gives the same products obtained from the reaction in neat MeCN, viz the 1-(*p*-methoxybenzyl)-naphthalene 5c and the *p*-(methoxybenzyl)dihydronaphthalenes 2c, 3c, and 9c, though with a marked shift of the yields in favor of the 1-substituted dihydronaphthalene 2c. Under the  $\gamma$  conditions the benzylated naphthalenes 5c and 6c are obtained in low yields. The main product in this case is the mononitrile 7. Here again, 1,2-bis(4-methoxyphenyl)ethane is formed under all conditions.

Finally, the reaction of NDN with benzyltrimethylsilane (1d) is essentially unaffected by changing the medium from MeCN to MeCN–MeOH. Two benzylidihydronaphthalenes 2a and 3a are formed in the same yield under both conditions. Under the  $\gamma$  conditions the reaction remains clean, contrary to the previous cases, and the two benzylidihydronaphthalenes, 5a and 6a, are obtained in good yields. Traces quantities of bibenzyl are formed in each case.

In order to gain information about the origin of the products in these photoreactions a series of experiments were carried out. First, the benzylic donors were omitted from the reaction mixtures. Thus, irradiation of NDN in MeOH or 0.1 M KOH in MeOH does not cause appreciable reaction on the time scale of the previous experiments, nor does it result in the formation of any of the products described above.

Second, the stability of the photoproducts to base was checked. Treatment of methanolic solutions of the benzylidihydronaphthalenedicarbonitriles 2a–c and 3a–c with KOH at 25 °C causes dehydrocyanation to yield the benzylidihydronaphthalenecarbonitriles 5a–c and 6a–c, respectively. Likewise, the alcohol 4 undergoes dehydrocyanation to yield the naphthalene 8. In the case of the 2-substituted derivatives 3a,b a minor path involving dehydrogenation to 11 (oxygen was not excluded in these experiments) (Scheme 3) is followed. A more complicated course is followed in the reaction of the benzhydryl derivatives. Thus, treatment of 2b and 3b with KOH causes dealkylation to give NDN competitively with dehydrocyanation to yield 5b and 6b. Product 10 is hydrolyzed under this condition to yield a stable dibenzotetralone. All products undergo further reactions when irradiated in MeCN–MeOH or MeCN–MeOH–PhCH<sub>3</sub>. However, in the experiments reported above the irradiation is interrupted when some NDN (absorbing most of the light) is still present, and secondary photoreactions occur only to a limited extent.

**Table 2. Quantum Yields for the Photoreaction of NDN in the Presence of Benzylic Donors**

donor	conditions <sup>a</sup>		
	$\alpha$	$\beta$	$\gamma$
1a, 0.2 M	0.07	0.04	0.008
1b, 0.1 M	0.035	0.075	0.012
1c, 0.05 M	0.035	0.005	0.003
1d, 0.05 M	0.25	0.18	0.13

<sup>a</sup> See Table 1.

Finally, the quantum yields for the photoreactions of NDN under conditions  $\alpha$ – $\gamma$  with the above donors were measured (Table 2).

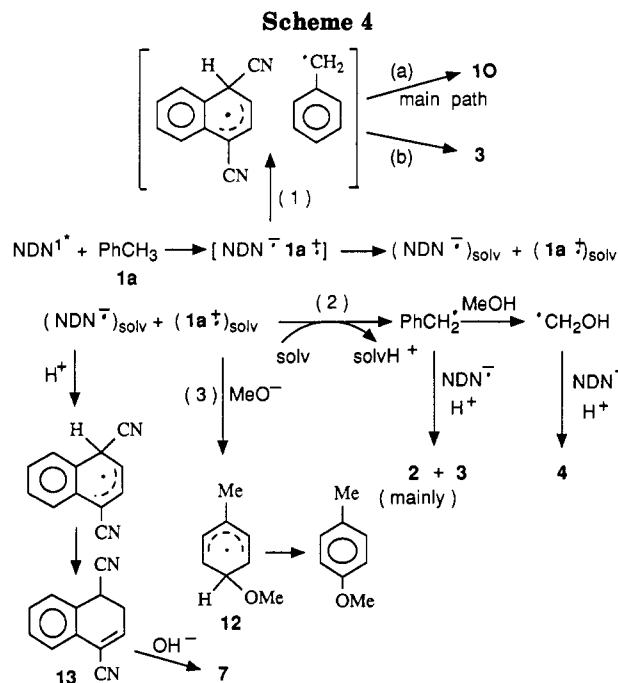
## Discussion

The aim of this study was to obtain information about the chemistry of radical ions and its alteration by changes in the medium. The radical ion intermediates were generated by photoinduced electron transfer from benzylic donors to the singlet excited state of the cyanoarene NDN.<sup>3</sup> That electron transfer occurs in these systems is evidenced by the fact that all of the benzylic donors studied quench the fluorescence of NDN. This is expected based on the predicted<sup>3</sup> thermodynamic/kinetic facility of SET in these donor–acceptor pairs.

Furthermore, changes in the medium have no dramatic effect on the NDN singlet state quenching by these donors. Indeed, NDN fluoresces with lower efficiency in MeCN–MeOH compared to neat MeCN, probably due to a decrease of  $\tau_s$ . But this change does not preclude efficient quenching of NDN by the aromatic derivatives in MeOH–MeCN. The problem is more serious for the experiments under basic conditions, since here the hydroxide competes as a donor with the benzylic compounds, especially in the case of 1a and 1b which have low  $K_{sv}$  values. This reduces the fraction of NDN singlets intercepted by the benzylic donors (with KOH in MeCN–MeOH the  $K_{sv}$  for the quenching of NDN fluorescence is 25 M<sup>-1</sup>). This is not an important factor however with 1c and 1d which have  $K_{sv}$  values >100 M<sup>-1</sup>. At any rate, since none of the reactions reported here (including hydroxymethylation and decyanation) occur in the absence of the benzylic donors, quenching by the base at most causes a lowering of the quantum yield, as indeed we observe. Furthermore, the presence of the base does not hinder the detection of NDN alkylation since in its presence the adducts are transformed into well-recognized compounds, e.g. dihydro dinitriles are converted to the rearomatized mononitriles (although with partial dealkylation in the case of the benzhydryl derivatives).

Since electron donation always occurs from the aromatic ring of the benzylic donors under all conditions, any changes in the chemistry engendered by changes in reaction conditions must be a result of alterations in the reactivity of the benzylic radical cations or NDN anion radicals. In the following paragraphs we will discuss separately the reactions involving deprotonation (donors 1a–c) and those involving desilylation (donor 1d) of the intermediate cation radicals and how these processes are controlled by the medium.

**Deprotonation of the Benzylic Radical Cations.** We suggest that the effect of the medium on the photochemical reaction between NDN and toluene is due to the occurrence of three different paths for the toluene radical cation (see Scheme 4).



**Route 1.** This predominates in neat acetonitrile. It has been previously demonstrated<sup>3</sup> that under this condition the reaction proceeds via proton transfer from the cation radical to the NDN anion radical in the original radical ion pair. This is followed by coupling of the resulting radicals within the solvent cage to yield the tetracyclic derivative 10 as the main product (route 1a) and the 2-benzylidihydronaphthalene 3a as the minor one (route 1b). The origin of the products benzylated in route 1 (2a and 5a) under this condition is due to the occurrence of some out-of-cage deprotonation of the toluene radical cation (route 2, see below), as shown also by the formation of some bibenzyl.

**Route 2.** When the medium is changed to methanol-acetonitrile 1:1, reaction by the above route is strongly attenuated. This effect appears to be due to an enhanced separation of the radical ions induced by MeOH not so much because of the increase in polarity, but rather as a result of the specific solvation of both radical ions by this protic and nucleophilic solvent. The cleavage of the benzylic radical cation now occurs at the free ion state, and the proton is transferred to the alcohol. Consequently, the carbon-carbon bond-forming step involves reencounter of the benzyl radical with the NDN radical anion. The latter species may accumulate under this condition since it has no fast monomolecular decomposition pathway available and it is a reasonably nonbasic species.<sup>11</sup> In this free radical encounter route, benzylation occurs predominantly at position 1 of the naphthalene ring, viz. at the position of larger spin density in the radical anion, as consistently observed in other alkylations occurring through

the radical-radical anion addition mechanism.<sup>1c,3f</sup> Addition of the benzyl radical to the NDN anion radical competes with hydrogen abstraction by this radical from methanol, which yields a hydroxymethyl radical. This in turn couples with the NDN radical anion to yield the alcohol 4. This observation provides alternate evidence for the role of the free benzyl radical in photoreactions occurring under this condition.<sup>12</sup>

**Route 3.** For the reaction of NDN with toluene in the presence of KOH, a low quantum yield is observed because of the competitive unproductive quenching of  $\text{NDN}^{1+}$  by the hydroxide anion. It is more difficult to draw mechanistic conclusions for condition  $\gamma$ , since the material balance is low. The product distribution changes conspicuously, with the benzylated product reduced to trace amounts. Indeed, an alternative path for the toluene radical cation has been identified in this case, and it is nucleophile addition with  $^-\text{OMe}$  to yield radical 12 in competition with deprotonation (route 3). There is precedent for the addition of nucleophiles to olefinic<sup>2b,13 a,b</sup> and aromatic<sup>13c,d</sup> radical cations to give neutral radicals. Such radicals have been shown to add to cyanobenzene radical anions;<sup>13</sup> however, we have found no evidence for formation of methoxyphenylated naphthalene in the present study. Apparently, a major reaction of 12 is rearomatization to produce methoxytoluene. Further paths are surely operating, leading e.g. to quinones or polymers; this probably explains that the solution becomes dark in this case (and not in the absence of the base) and that isolated yields are poor. At any rate, the concentration of benzyl radicals is diminished and therefore benzylation of NDN is inefficient. However, the presence of benzyl radicals as intermediates is shown by the isolation of some bibenzyl and by the occurrence of hydroxymethylation of NDN (the  $\dot{\text{C}}\text{H}_2\text{OH}$  radical is formed from route 2). Noteworthy, a further process involving NDN occurs in the presence of bases, viz. decyanation to produce 7. This is probably due to reduction to give the dihydro dinitrile 13 followed by dehydrocyanation to yield 7.

The same mechanisms are operating in the reaction of NDN with the other donors where proton transfer is involved (viz. with 1b and 1c), with some change induced by the donor structure. The occurrence of route 1 requires that the acceptor and the donor remain in a tight complex for the entire reaction sequence (proton transfer followed by formation of the two  $\sigma_{\text{C-C}}$  bonds and hydrogen transfer). Thus, steric and electronic factors destabilizing this complex would have an adverse effect on the process.

The influence of steric factors is revealed by the reaction with diphenylmethane (1b) where quantum yield is lower and only the 2-alkylated dihydronaphthalene 3b and no tetracyclic adduct is formed (path 1b). Our rationalization for this is that proton transfer does occur in the contact

(11) (a) It is known that the radical anions of aromatics are poor bases, see e.g. ref 11b; in the photoinduced SET reactions of aromatic nitriles, it is generally assumed that the concentration of the stable radical anion of those molecules grows during the irradiation when the radical cation is consumed through a fast chemical reaction and is thus subtracted to back electron transfer, see e.g. ref 11c,d. Spectacular evidence for the stability of the radical anion of an arenecarbonitrile (in the presence of water!) has been recently obtained, see ref 11e. (b) Zimmerman, H. E.; Wang, P. A. *J. Am. Chem. Soc.* 1990, 112, 1280. (c) Lan, J. Y.; Schuster, G. B. *Tetrahedron Lett.* 1986, 27, 4261. (d) Popielartz, R.; Arnold, D. R. *J. Am. Chem. Soc.* 1990, 112, 3068. (e) Kellet, M. A.; Whitten, D. G.; Gould, I. R.; Bergmark, W. R. *J. Am. Chem. Soc.* 1991, 113, 358.

(12) Alternatively, it can be that in the MeOH-MeCN solution two processes are operating. In the former one the benzylic proton is transferred to the alcohol directly from the geminate ion pair and the radical-radical anion pair combines to give the anionic adduct (compare Scheme 5, eq 7), while in the second mechanism the fraction of radical cations diffusing and deprotonating out of cage abstracts a hydrogen from methanol, and thus only the hydroxymethyl radical attacks  $\text{NDN}^-$  through the reencounter mechanism. This alternative is compatible with the general scheme proposed here.

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ion radical pair (route 1), but the bulky and stabilized benzhydryl radical causes cage escape to be faster than in the previous case (hence the lower  $\phi$ ) and furthermore a change in the mode of radical pair coupling, so that now one-bond formation to give **3b** predominates over two-bond formation to give **10** (route 1b rather than route 1a).

In the photoreaction of **1b** with NDN in MeCN–MeOH deprotonation occurs as before out of cage, and alkylation involves recombination of the radical intermediates (route 2). In accordance with this rationalization, attack at position 1 (to give **2b**) rather than 2 (to give **3b**) is favored, and furthermore hydrogen abstraction from methanol also occurs, leading to hydroxymethylation of NDN. As before, some free radical coupling to yield 1,1,2,2-tetraphenylethane occurs under all conditions. In the presence of bases the only NDN-derived products are, as with **1a**, **7** and **8**.

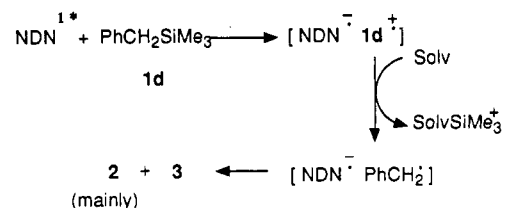
The influence of electronic factors is apparent in the SET-induced reaction of **1c**: in this case, separation from the contact ion radical pair is favored as a consequence of the stability of radical cation **1c<sup>+</sup>**. Furthermore, since a large degree of positive charge density in **1c<sup>+</sup>** is on the methoxy oxygen, the initial radical ion complex probably has a different conformation from the previous cases. These two factors may account for why the quantum yield is remarkably lower here than in the toluene case, since deprotonation occurs mainly through the slow out-of-cage path. The difference in product distribution between condition  $\alpha$  (larger proportion of benzylation in **2**) and condition  $\beta$  may indicate that some in-cage proton transfer and radical–radical coupling (route 1b) occur in neat MeCN, while obviously only route 2 is followed under condition  $\beta$ . In contrast to the previous cases, however, the free *p*-methoxybenzyl radical is more stabilized. Thus, it behaves as a poor alkylating agent (the quantum yield for benzylation of NDN remain low under all conditions), it is apparently unable to abstract hydrogen from methanol (no hydroxymethylation of NDN in reaction conducted under the  $\beta$  or  $\gamma$  condition) and does not add methoxide (route 3). Under condition  $\gamma$  reduction and dehydrocyanation of NDN to give **7** are the main path, though again with a low quantum yield.

**Desilylation.** In complete contrast with the other processes, the reaction of the benzylsilane **1d** shows very little dependence on the medium, both in terms of the overall quantum yield and the product distribution. The fact that no hydroxymethylation takes place under conditions  $\beta$  and  $\gamma$  with **1d** proves that no free benzyl radicals are involved. This is also shown by the minimal formation of bibenzyl. Thus, desilylation occurs very rapidly before radical ion separation and the benzyl radical thus formed directly combines with NDN<sup>-</sup>. Since this is a radical–radical anion combination, the regiochemistry is as usual in favor of position 1 of the cyanoarene ring.

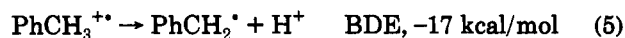
**Mechanism of the Radical Cation Cleavage.** There has been much attention given in the recent literature to the mechanism of radical cation cleavage (eq 2). Thermochemical cycles allow one to calculate the bond dissociation energy (BDE) of the radical cation when the potential for the X<sup>•</sup>/X<sup>+</sup> equilibrium is known. On this basis one obtains that deprotonation of the toluene radical cation is an exothermic process,<sup>3d,14,15</sup> while desilylation

(14) (a) Wayner, D. D. M.; Dannenberg, J. J.; Griller, D. *Chem. Phys. Lett.* **1986**, *131*, 189. (b) Wayner, D. D. M.; McPhee, D. J.; Griller, D. *J. Am. Chem. Soc.* **1988**, *110*, 132.

Scheme 5

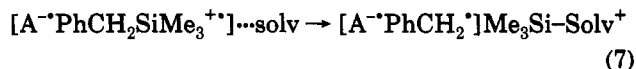


of **1d<sup>+</sup>** confronts a sizeable barrier.<sup>3f,7a</sup>



The energy barrier associated with the process in eq 6 is too high to make an unimolecular fragmentation fast enough to compete with back electron transfer (see e.g. in the discussion by Dinnocenzo et al.<sup>7a</sup>). This rationalization would require some discussion since this BDE is calculated on the basis of the appearance potential of the MeSi<sub>3</sub><sup>+</sup> cation in the mass spectrum<sup>16</sup> and, as such, refers to the gas phase. This is not a good model for solution reactions when the involved radical cation and cation largely differ in their structure.<sup>17</sup> Here the former one is a  $\pi$ -delocalized and the latter one a localized species). Our results show that the yield of bibenzyl from the reaction of **1d<sup>+</sup>** is very low even under conditions  $\beta$  and  $\gamma$ , which favor free radical formation. This suggests that out-of-cage desilylation is unimportant in these processes.

At any rate neither in the Dinnocenzo case,<sup>7a</sup> in the present reactions, nor in related reactions involving desilylation of a radical cation<sup>18</sup> is the quantum yield for the alkylation of the acceptor affected by the medium character. Therefore, while it is obvious that the silyl cation is not set free in the fragmentation of **1d<sup>+</sup>**, but rather transferred to a convenient acceptor, it is clear that MeCN is a sufficiently good nucleophile to make the fragmentation process (desilylation) faster than diffusional collapse of the ion radical pair (see eq 7, Scheme 5).



In contrast, benzylic deprotonation of cation radicals, although thermodynamically favored, proceeds at a slow rate. The formation of the tetracyclic derivative **10** from NDN and **1a** in MeCN is due to proton transfer within the geminate pair. The fact that such a reaction occurs at all is due to the strong interaction of the donor and the acceptor in the contact ion pair (or strongly polarized exciplex; here the  $\Delta G_{\text{et}}$  is only slightly negative).

(15) Nicholas, A. M. P.; Arnold, D. R. *Can. J. Chem.* **1982**, *60*, 2165.

(16) Hess, G. G.; Lampe, F. W.; Sommer, L. H. *J. Am. Chem. Soc.* **1965**, *87*, 5237.

(17) (a) Actually, in a number of cases it has been found that fragmentation energies for radical cations differ by less than 4 kcal mol<sup>-1</sup> in the gas phase and in solution, see ref 17b. In all the cases studied, however, both the radical cation and the cation formed from the cleavage are  $\pi$ -delocalized species, and therefore the two solvation energy terms cancel out. This is not likely to be the case when, as with the present substrates, the radical cation is a  $\pi$ -delocalized species and the cation a localized species, arguably with largely different solvation energies. (b) Griller, D.; Simoes, J. A. M.; Mulder, P.; Sim, B. A.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1989**, *111*, 7872.

(18) Ohga, K.; Yoon, U. C.; Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 213.

A further element highlighted by the present study is the competitive addition of different radicals to the NDN radical anion. Thus, when deprotonation takes place out of cage, the alkylation step occurs on reencounter of the benzyl radical and  $\text{NDN}^{\cdot-}$ . We have no means for assessing the rate of this reaction, since the steady-state concentration of the two species is not known. At any rate, with MeOH as cosolvent there is sufficient time for hydrogen abstraction to occur. The radical character of  $\text{NDN}^{\cdot-}$  probably makes it react with any radical at the diffusion-controlled rate, independent of its electronic character, leading to the formation of both the benzylated and the hydroxymethylated naphthalenes.

**Conclusions.** The present work contributes information about some issues related to the chemistry of radical cations and the mechanism of the PET-induced alkylation of aromatics. In previous work on the alkylation of NDN driven by the intramolecular competitive fragmentation of xylene derivatives in MeOH–MeCN we showed that desilylation is at least 100 times faster than deprotonation.<sup>4b</sup> The present data afford direct evidence for the timing of bond-making and -breaking in the process leading from the radical ion pair to the final alkylated derivatives. The silyl cations are excellent electrofugal groups. Thus, even in the presence of weak nucleophiles like acetonitrile, silyl transfer occurs from the geminate pair. On the contrary, deprotonation from the benzylic position is slow, although proton transfer within the radical ion pair occurs efficiently. In the out-of-cage reaction, the toluene radical cation undergoes nucleophile addition on the ring, competitive with nucleophile-assisted deprotonation. Free benzylic radicals abstract hydrogen from methanol, competitive with their addition to  $\text{NDN}^{\cdot-}$ . As for the NDN alkylation, attack at position 1 is largely preferred when it involves a radical–radical anion addition (independent from the fact that fragmentation of the radical cation to the radical occurs from the radical ion pair from the free radical cation). From the synthetic point of view, this study shows the limitations of PET alkylation for the functionalization of aromatics, but also some new possibilities, e.g. alkylation with “secondary” radicals. Finally, one should emphasize that, while a cleaner picture of the chemistry of photogenerated radical ions has been obtained in this case, the above mechanistic conclusions refer only to the presently considered system, where both the donor and the acceptor are aromatic molecules and the reaction involves the singlet state. The mechanism operating when there are different acceptors (e.g. ketones, acting through their triplet state, and much better nucleophiles than arenecarbonitriles) and different donors (e.g.  $n$  or  $\sigma$  donors are involved) need not be the same.

### Experimental Section

1,4-Naphthalenedicarbonitrile (NDN) was prepared and purified as previously described. The benzylic derivatives used were commercial products and were purified by fractional distillation. Spectrograde solvents (Carlo Erba) were used as received. All photochemical reactions were performed using Ar purged 1:1 MeCN–MeOH solution (100 mL; when required, a methanolic solution of KOH was used) of NDN (120 mg, 0.67 mmol) containing the arene substrate in an immersion well apparatus with a 150-W medium-pressure mercury arc and Pyrex glass filter. Workup of the photolysates involved concentration in vacuo (after neutralization with  $\text{NH}_4\text{Cl}$  in the case of the basic solutions) and column chromatographic separation using Merck

type 60 (230–400 mesh) silica gel. The yields recorded for the photoaddition are based on consumed NDN.

**Photoreaction of NDN with Toluene (1a).** Irradiation for 3 h of a solution of NDN (120 mg, 0.67 mmol) and toluene (1.5g, 16.3 mmol) followed by workup and silica gel chromatography (cyclohexane–EtOAc) under the general conditions described above gave beside 20 mg of unreacted NDN, 9 mg (6%) of 1-benzyl-1,2-dihydro-1,4-naphthalenedicarbonitrile (2a),<sup>3a</sup> traces (ca. 1%) of the 2-benzyl isomer 3a,<sup>3a</sup> and 35.4 mg (30%) (mp 118–9 °C, benzene–cyclohexane) of 1-(hydroxymethyl)-1,2-dihydro-1,4-naphthalenedicarbonitrile. Analysis by VPC (confirmed by GC–MS) showed that 15 mg of bibenzyl had been formed. Irradiation for 3 h of a similar solution, now 0.1 M in KOH, followed by workup and silica gel chromatography as above gave, besides 35 mg of unreacted NDN, traces of the 4- and 3-benzyl-naphthalene-1-carbonitrile (5a, 6a),<sup>3a,6b</sup> 6 mg (8%) of 1-naphthalenecarbonitrile (7), and 13 mg (15%) (mp 99–100 °C, benzene–cyclohexane) of 4-(hydroxymethyl)-1-naphthalenecarbonitrile (8). Other NDN-derived products, probably dibenzylated derivatives, were also present. Analysis by VPC, confirmed by GC–MS showed the presence of 10 mg of bibenzyl and 30 mg of *p*-methoxytoluene.

4: <sup>1</sup>H NMR  $\delta$  2.97 (dd,  $J = 18.0$  and  $3.5$  Hz, 1H, ABX  $\text{CH}_2$ ), 3.27 (dd,  $J = 18.0$  and  $6.5$  Hz, 1H, ABX  $\text{CH}_2$ ), 3.7 (2H, AB  $\text{CH}_2\text{-OH}$ ), 6.8 (dd,  $J = 6.5$  and  $3.5$  Hz, 1H, C=CH), 7.5 (m, 2H, arom), 7.6 (m, 1H, arom), 7.65 (m, 1H, arom). Anal. Calcd for  $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}$ : C, 74.27; H, 4.79; N, 13.33. Found: C, 74.05; H, 4.80; N, 13.20.

8: <sup>1</sup>H NMR  $\delta$  5.28 (s, 2H,  $\text{CH}_2\text{OH}$ ), 7.67 (d,  $J = 7$  Hz,  $\text{H}_3$ ), 7.92 (d,  $J = 7$  Hz,  $\text{H}_2$ ), 7.7 (m, 2H,  $\text{H}_6$  and  $\text{H}_7$ ), 8.12 (dd,  $J = 8$  and  $1.5$  Hz,  $\text{H}_5$ ), 8.28 (dd,  $J = 8$  and  $1.5$  Hz,  $\text{H}_5$ ). Anal. Calcd for  $\text{C}_{12}\text{H}_9\text{NO}$ : C, 78.67; H, 4.95; N, 7.65. Found: C, 78.35; H, 4.85; N, 7.50.

**Dehydrocyanation of Adducts 2a, 3a, and 4.** The photoadduct 2a (30 mg, 0.11 mmol) was dissolved in 5% KOH in ethanol (10 mL). After 1 h the mixture was diluted with saturated aqueous  $\text{NH}_4\text{Cl}$  and extracted with  $\text{CH}_2\text{Cl}_2$ . Evaporation of the organic layer after drying and recrystallization gave the naphthalene 5a (18 mg, 67%). Similar treatment of adduct 3a (60 mg, 0.22 mmol) followed by silica gel chromatography gave the naphthalenes 6a (23 mg, 43%) and 11a (16 mg, 27%) (mp 117–20 °C). Similar treatment (for 3 h) of adduct 4 (30 mg, 0.15 mmol), followed by silica gel chromatography, gave 8 (15 mg, 58%).

11a: <sup>1</sup>H NMR  $\delta$  4.45 (s, 2H,  $\text{CH}_2$ ), 7.3 (s, 5H, Ph), 7.8 (s, 1H,  $\text{H}_3$ ), 7.75–7.95 (m, 2H) and 8.2–8.4 (m, 2H) (arom); IR: 2220  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{19}\text{H}_{12}\text{N}_2$ : C, 85.5; H, 4.51; N, 10.44. Found: C, 84.7; H, 4.7; N, 10.1.

**Photoreaction of NDN with Diphenylmethane (1b).** Irradiation for 6 h of a solution of NDN (120 mg, 0.67 mmol) and diphenylmethane (1b) (1.5 g, 16.3 mmol) in 100 mL of 1:1 MeOH–MeCN followed by workup and chromatography under the general conditions described above gave, besides 35 mg of unreacted NDN, 25 mg (15%) (mp 45–50 °C) of 1-(diphenylmethyl)-1,2-dihydro-1,4-naphthalenedicarbonitrile (2b), 8 mg (5%) and 3 mg (2%) respectively of the two isomeric 2-diphenylmethyl derivatives (3b and 9b),<sup>3d</sup> and the alcohol 4. Irradiation for 5 h of a similar solution, now 0.1 M in KOH, followed by workup as above gave, besides 5 mg of unreacted NDN, 15 mg (15%) of the nitrile 7 and 12 mg (10%) of the alcohol 8.

2b: <sup>1</sup>H NMR  $\delta$  3.0 (ABX, 2H,  $\text{CH}_2$ ), 4.1 (s, 1H,  $\text{CHPh}_2$ ), 6.67 (dd,  $J = 5.5$  and  $4$  Hz, 1H, C=CH), 6.85–7.8 (m, 14H, arom). Anal. Calcd for  $\text{C}_{25}\text{H}_{18}\text{N}_2$ : C, 86.67; H, 5.24; N, 8.09. Found: C, 86.30; H, 5.15; N, 7.85.

**Dehydrocyanation of Adducts 2b and 3b.** The photoadduct 2b (30 mg, 0.09 mmol) was dissolved in 5% KOH in ethanol. After 3 h the mixture was concentrated, diluted with saturated aqueous  $\text{NH}_4\text{Cl}$ , and extracted with  $\text{CH}_2\text{Cl}_2$ . Evaporation of the organic layer and silica gel chromatography gave NDN (2 mg, 13%) and 5b (18 mg, 65%) (mp 156–59 °C). Treatment of adduct 3b (30 mg, 0.09 mmol) in the same way gave NDN (2 mg, 13%), 6b (21 mg, 76%) (mp 143–45 °C), and a trace of a product showing the UV and MS ( $m/z$  344) characteristics expected for 11b.

5b: <sup>1</sup>H NMR  $\delta$  6.3 (s, 1H,  $\text{CHPh}_2$ ), 7–7.4 (m, 10H, arom), 7.55 and 7.65 (2m, 1H each, arom  $\text{H}_6$  and  $\text{H}_7$ ), 7.8 (d,  $J = 7$  Hz, 1H, arom  $\text{H}_3$ ), 7.95 (d,  $J = 7$  Hz, arom  $\text{H}_2$ ), 8.1 (dd,  $J = 8$ , 1.5 Hz, 1H, arom  $\text{H}_5$ ), 8.3 (dd,  $J = 8$ , 1.5 Hz, 1H, arom  $\text{H}_5$ ); IR 2220  $\text{cm}^{-1}$ . Anal.

Calcd for  $C_{24}H_{17}N$ : C, 90.25; H, 5.37; N, 4.39. Found: C, 90.05; H, 5.25; N, 4.2.

**6b:**  $^1H$  NMR  $\delta$  5.75 (s, 1H,  $CHPh_2$ ), 7.25 (s, 1H,  $H_2$ ), 7.8 (s, 1H,  $H_4$ ), 7.1–7.4 (m, 10H, arom), 7.6–7.9 (m, 3H, arom), 8.2 (dd,  $J = 2, 8$  Hz, 1H,  $H_3$ ); IR, 2220  $cm^{-1}$ . Anal. Calcd for  $C_{24}H_{17}N$ : C, 90.25; H, 5.37; N, 4.39. Found: C, 90.2; H, 5.35; N, 4.2.

**Photoreaction of NDN with *p*-Methoxytoluene (1c).** Irradiation for 8 h of a 1:1 MeOH–MeCN solution of NDN (100 mg) and *p*-methoxytoluene (1c) (1g, 9.3 mmol) followed by workup and chromatography by using the general conditions described above gave, besides 35 mg of unreacted NDN, 28.5 mg (23%) of the rearomatized (*p*-methoxybenzyl)naphthalene **5c**,<sup>3g</sup> 79 mg (58%) of the 1-benzylidihydronaphthalene **2c**,<sup>3g</sup> 11 mg (8%) and 3 mg (2%), respectively, of the two isomeric 2-benzyl derivatives **3c** and **9c**.<sup>3g</sup> Irradiation for 8 h of a similar solution, now 0.1 M in KOH, followed by the workup as above gave, besides 40 mg of unreacted NDN, 15 mg (13%) and 2 mg (2%), respectively, of the 4- and the 3-(*p*-methoxybenzyl)naphthalene-1-carbonitrile (**5c** and **6c**),<sup>5c</sup> as well as 27.5 mg (40%) of 1-naphthalenecarbonitrile (**7**) and 20 mg of 4-amino-1-naphthalenecarbonitrile. Description of the formation of the last compound in this and related reactions will be reported separately.

**Dehydrocyanation of Adducts 2c and 3c.** The adduct **2c** (30 mg, 0.1 mmol) was dissolved in 5% KOH in ethanol (20 mL). After 2 h the mixture was concentrated, diluted with saturated aqueous  $NH_4Cl$ , and extracted with  $CH_2Cl_2$ . Evaporation of the

solvent after drying and recrystallization of the residue gave the naphthalene **5c** (22 mg, 80%). Treatment of **3c** under the same conditions gave **6c** (15 mg, 55%).

**Photoreaction of NDN and Benzyltrimethylsilane (1d).** Irradiation for 40 min of a solution of NDN (120 mg, 0.67 mmol) and benzyltrimethylsilane (0.5 g, mmol) followed by workup and chromatography as above gave, besides 5 mg of unreacted NDN, 125 mg (72%) of **2a** and 43 mg (25%) of **3a**. Irradiation for 40 min of a similar solution, now 0.1 M in KOH, and workup as above gave, besides 5 mg of unreacted NDN, 102 mg (65%) of the 4-benzyl naphthalene **5a** and 28 mg (18%) of the 3-benzyl isomer **6a**.

**Quantum Yield Measurements.** Reaction quantum yields were measured on degassed (through four freeze-degas-thaw cycles)  $10^{-4}$  M solutions of DCN in 1-cm optical path cuvettes on an optical bench. Light intensity from an Osram 200-W high-pressure mercury arc lamp was focused and monochromatized by means of an interference filter ( $\lambda_{max}$  313 nm). Light intensity was measured by ferrioxalate actinometry. An absorbed flux of ca  $10^{-7}$  Einstein  $min^{-1} cm^{-2}$  was measured.

**Fluorescence Measurements.** Fluorescence measurements were made on degassed  $10^{-5}$  M solutions of DCN by means of an Aminco-Bowman MPF spectrofluorimeter.

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