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Photochemical Reaction between 1,4-Naphthalenedicarbonitrile and α-Substituted Benzylic Derivatives

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Abstract: The photochemical reaction of 1,4-naphthalenedicarbonitrile (NDN) with benzylic derivatives of the general formula PhCHRX (R = H, Ph; X = H, C, O, S, Si, Sn-bonded substituents) has been investigated. The competition between C–H and C–X bond cleavage in the photochemically created radical cation $PhCHRX^{\bullet+}$ is revealed by the different chemical products formed, viz. 5,11-methanodibenzo[*a,e*]cyclooctenes (**2**), from proton transfer and coupling of the radicals within the cage, and 2-benzyl- (**3**) and 1-benzyl-1,2-dihydronaphthalenes (**4**), as well as 4-benzyl-1-naphthalenenitriles (**5**), from the reaction between the radical anion $NDN^{\bullet-}$ and the neutral radicals $PhCHR^{\bullet}$ or $PhCRX^{\bullet}$. With the alcohols, the hydroxylic proton is easily transferred. Measurement of reaction quantum yield and fluorescence quenching and thermochemical calculations support the mechanism proposed.

The chemistry of photochemically created radical ions has been attracting a growing interest since the pioneering work by Arnold and other scientists.[1] We have been interested in the photochemical reaction between 1,4-naphthalenedicarbonitrile (NDN) and alkylbenzenes because of the new stereospecific reactions observed in this system.[7] Thus, when proton transfer from the benzylic position to the NDN radical anion takes place within the radical ion pair, an unprecedented radical–radical recombination involving the benzene ortho position ensues, leading stereospecifically to a tetracyclic derivative[7a,b] (product **2**, see Scheme I). If the proton is transferred to the medium, the reaction between the benzylic radical and the radical anion leads, again stereospecifically, to a *cis*-2-benzyl-1,2-dihydronaphthalene (**3**). The same type of product is formed when the benzyl radical arises from carbon–carbon cleavage in a bibenzyl radical cation.[7c] We further showed that stabilization of the radical cation, e.g. by substituting an electron-donating group in the ring, favors diffusion out of the cage of the radical ions and causes a decreased efficiency.[7b]

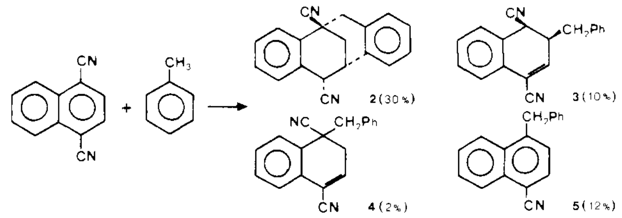
The present study is an effort to establish the scope of the reaction by examining the photochemical reaction of NDN with a series of benzyl (R = H) and benzhydryl (R = Ph) derivatives of the general formula PhCHRX. Since the sequence of the different steps of these reactions (e.g. proton transfer, formation of new carbon–carbon bonds) determines the type of end-products obtained, it was expected that the effect of the substituting group X on benzylic deprotonation and the competition between cleavage of the C–H and the C–X bond in the radical cation should give useful mechanistic information.

Results

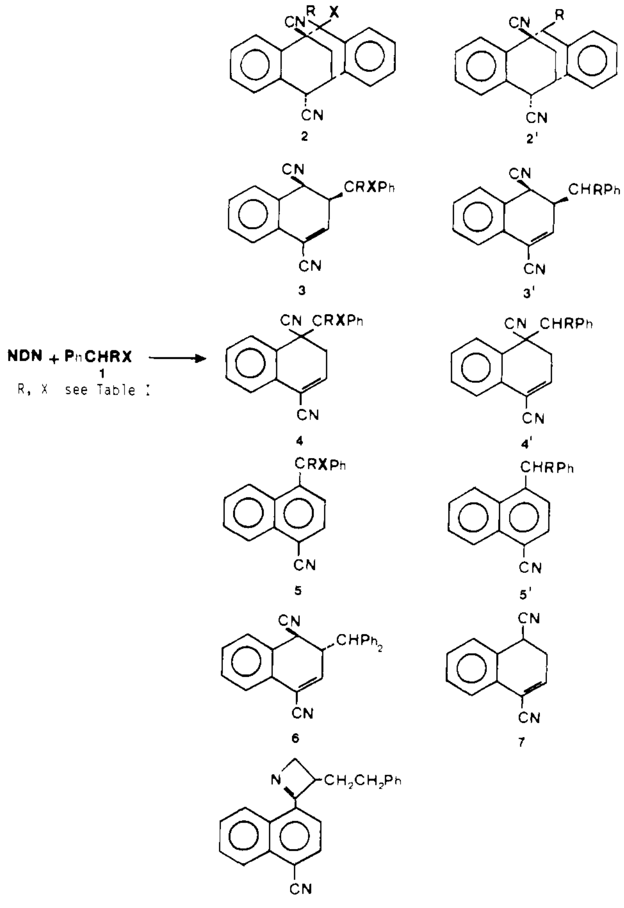
The donors examined in the present work correspond to the general formula PhCHRX and are listed in Table I. Scheme I shows the products obtained[7a] from the photoreaction of NDN with toluene for the sake of comparison. The results from the present work are gathered in Table I and in Scheme II, where unprimed and primed numbers label adducts resulting from the detachment of a hydrogen or, respectively, of a group X in the benzylic donor. Three classes of donors PhCHRX were considered besides diphenylmethane, which, together with the previously considered toluene,[7] serves as a reference compound (X = H) for the three series.

Irradiation of NDN in acetonitrile in the presence of diphenylmethane (**1a**) causes some oxidation of the donor to

Scheme I



Scheme II



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(1) For some leading references, see ref 2–6.

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Table I. Chemical Products from the Photoreaction of NDN with Benzyl Derivatives of the General Formula PhCHRX (**1**)

substrate	substituents		
1	R	X	products (% yield)
a	Ph	H	**3a** (45), **6a** (11), **7** (traces), $Ph_2CHCHPh_2$, Ph_2CO
b	Ph	$CHPh_2$	**3a** (57), Ph_2CH_2, Ph_2CO
c	Ph	CH_2OMe	*a*
d	H	CH_2OMe	*a*
e	CH_2	CH_2	*a*
f	H	$CH_2CH{=}CH_2$	**4f** (8), **4′f** ≡ 4 (traces), **7** (40), **8** (15)
g	H	$CH{=}CH_2$	*a*
h	H	*t*-Bu	**2h** (7), **2′h** ≡ **2** (17), **5** (12), **5′h** ≡ **5** (14), **7** (traces)
i	Ph	Cl	*b*
j	Ph	COOMe	*b*
k	Ph	CN	*b*
l	Ph	OH	**3l** (14), **7** (28), $Ph_2C(OH)CPh_2OH$, Ph_2CO
m	Ph	OMe	**7** (40), Ph_2CO, Ph_2CH_2
n	H	OH	**7** (68), PhCHO
o	H	OMe	**4o** (72), **7** (8), PhCH(OMe)CHPhOMe
p	H	SMe	**4p** (43) **7** (traces), PhCH(SMe)CHPhSMe
q	H	$SiMe_3$	**3′q** ≡ **3** (30), **4′q** ≡ **4** (70)
r	H	$SnBu_3$	**3′r** ≡ **3** (20), **4′r** ≡ **4** (30), **5′r** ≡ **5** (39)

[a] Complex mixture of photoproducts. [b] No photochemical reaction.

1,1,2,2-tetraphenylethane and reduction of the acceptor to 1,2-dihydro-1,4-naphthalenedicarbonitrile (**7**), but the major reaction leads to two stereoisomeric adducts, viz. *cis*-2-(diphenylmethyl)-1,2-dihydro-1,4-naphthalenedicarbonitrile (**3a**) and the corresponding trans derivative **6**, easily identified from their spectroscopic properties (e.g., different $J_{1,2}$ in ^1H NMR, preferential HCN vs H_2 elimination from the molecular ion in the mass spectrum; the identification of the new products is discussed in the Experimental Section). Compound **3a** is the main product in this case, and it is also the only adduct obtained from the reaction of NDN with 1,1,2,2-tetraphenylethane (**1b**).[7c] In that case, formation of this product involves fragmentation of the carbon–carbon bond in the radical cation according to eq 1. This

$$Ph_2CHCHPh_2^{\bullet +} \rightarrow Ph_2CH^{\bullet} + Ph_2CH^{+} \qquad (1)$$

easy fragmentation is due to the stabilization of both benzyl radical and cation, as it has been pointed out also by other groups.[8]

Compound **1b** is an example of the first class of donors considered, in which the group X corresponds to a stable carbon-centered cation. In the case of diphenylethyl methyl ether (**1c**) it is known that a similar fragmentation occurs (eq 2), as established in previous work through methanol trapping.[9] We irradiated NDN with both **1c** and phenylethyl methyl ether (**1d**) with no methanol added, and found that the nitrile is consumed and a complex mixture of products in low individual yield is formed.

$$Ph_2CHCH_2OMe^{\bullet +} \rightarrow Ph_2CH^{\bullet} + CH_2{=}O^{+}Me \qquad (2)$$

These do not include product **3a** or, respectively, the corresponding monophenyl derivative, which would be expected from the reaction of the benzhydryl or benzyl radicals and $NDN^{\bullet -}$. A similar situation was observed with phenylcyclopropane (**1e**), known to undergo cleavage of the ring under similar conditions,[10] and we were unable to isolate the numerous products formed in low yield.

A clean reaction takes place with 4-phenylbutene (**1f**) and yields reduced NDN (**7**) as well as three products involving addition between the donor and the acceptor, viz. the azetine **8** arising from 2 + 2 addition of the alkene double bond onto a cyano group and two 1-substituted 1,2-dihydronaphthalenes. One of these compounds results from addition of the donor with bond formation at the benzylic position (product **4f**); the other one (obtained in traces) involves previous fragmentation of a carbon–carbon bond in the donor, according to eq 3, loss of the allyl cation, and addition

$$PhCH_2CH_2CH = CH_2^{\bullet +} \rightarrow PhCH_2^{\bullet} + CH_2{=\!=}CH{=\!=}CH_2^{+} \qquad (3)$$

of the benzylic radical to yield product **4′f**. The reaction of 3-phenylpropene (**1g**) on the contrary is too complex.

With neopentylbenzene (**1h**), two pairs of products were obtained, viz. the two tetracyclic derivatives **2h** and **2′h** ≡ **2** arising respectively from direct addition of the donor and from addition after loss of the *tert*-butyl cation from the donor radical cation (eq 4) as well as the two naphthalenes **5h** and **5′h** ≡ **5** arising from

$$PhCH_2CMe_3^{\bullet +} \rightarrow PhCH_2^{\bullet} + CMe_3^{+} \qquad (4)$$

the substitution of the α-*tert*-butylbenzyl and of the benzyl radical, respectively, for one of the cyano groups. A minor product is the dihydro derivative **7**.

A second class of donors we considered includes benzylic derivatives containing substituents of strong inductive or mesomeric effect as the group X. NDN remained unchanged on irradiation in the presence of benzyl chloride (**1i**), methyl phenylacetate (**1j**) and phenylacetonitrile (**1k**), as well as of the corresponding benzhydryl derivatives (not listed in Table I).

A reaction is observed in the presence of benzhydrol (**1l**) and involves oxidation of the donor to benzopinacol and benzophenone, reduction of the acceptor to product **7**, and formation in 14% yield of the cis adduct in position 2 (product **3l**) as well as minor amounts of another unidentified adduct (see the Experimental Section). With benzhydryl methyl ether (**1m**), a slow reaction leads to consumption both of the nitrile, to yield product **7**, and of the donor, to yield benzophenone and diphenylmethane.

With benzyl alcohol (**1n**), the reaction leads essentially to benzaldehyde and **7**, and with benzyl methyl ether (**1o**), we previously reported[7d] formation of the adduct in position 1 (**4o**) along with reduction of NDN to **7** and oxidative dimerization of **1o** to the pinacol dimethyl ether. The irradiation with the corresponding thioether (**1p**) likewise causes a slow reaction with addition at position 1 (products **4p**, two diastereoisomers), reduction of NDN to **7** and oxidation of the donor to 1,2-diphenyl-1,2-dithioethane dimethyl ether.

Finally, we considered a third class of donors, viz. benzyl derivatives with a weak carbon–heteroatom C–X bond. These are benzyltrimethylsilane (**1q**) and benzyltri-*n*-butylstannane (**1r**). In both cases the reaction is fast and the group X is split off according to eq 5. Thus, the isolated products result from addition

$$PhCH_2M^{\bullet +} \rightarrow PhCH_2^{\bullet} + M^{+}\ (M = SiMe_3, SnBu_3) \qquad (5)$$

of the benzyl radical onto NDN in both positions 1 and 2 (products **4** and **3**, respectively) or substitution of the benzyl radical for a cyano group (product **5**), the former process predominating with the silane, the latter one with the stannane.[11a,b]

The preparative studies reported above have been supplemented by steady-state measurements, including quenching of the NDN fluorescence and chemical quantum yield at a fixed donor concentration (0.02 M) and, in selected cases, for a range of donor concentrations (see Table II). All the donors of the first class considered quench the fluorescence of the acceptor and react with low to moderate efficiency. In the second class, some of the donors (**1i–k**) neither quench nor react, while the other ones do both, though with largely different quantum yield, and the organometallic donors of the third class both quench and react efficiently.

Discussion

The general characteristics of the present reactions fall within the mechanistic scheme we previously proposed for the photo-

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[8] (a) Okamoto, A.; Arnold, D. R. *Can. J. Chem.* **1985**, *63*, 2340. (b) Okamoto, A.; Snow, M. S.; Arnold, D. R. *Tetrahedron* **1986**, *42*, 6175.

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[10] Mizuno, K.; Yoshioka, K.; Otsuji, Y. *Chem. Lett.* **1983**, 941.

[11] (a) In the meantime, the photochemical reaction between NDN and donors **1q** and **1r** has been reported by another group, ref 11b. (b) Mizuno, K.; Terasaka, K.; Yasueda, M.; Otsuji, Y. *Chem. Lett.* **1988**, 145. (c) Lan, J. Y.; Schuster, G. B. *J. Am. Chem. Soc.* **1985**, *107*, 6710. (d) Lan, J. Y.; Schuster, G. B. *Tetrahedron Lett.* **1986**, 4261.

Table II. Kinetic Parameters for the Photoreaction of NDN with Benzylic Donors

substrate **1**	K_{sv}, M^{-1} [a]	Φ (0.02 M)	Φ_{lim} [b]	K', M^{-1} [c]
1a	32	0.036	0.15	20
b	125	0.015	0.021	128
e	201	0.125		
f	15	0.06		
g	18	0.038		
j	<1	<0.001		
l	19	0.145	0.26	48
m	30	0.005		
n	12	0.05	0.07	30
p	164	0.005		
q	115	0.245	0.39	84
r	156	0.16		

[a] From fluorescence quenching. [b] Estrapolated from the Φ^{-1} vs [donor]$^{-1}$ plot. [c] Ratio between the intercept at the origin and the slope in the same plot.

chemical reaction between NDN and alkylbenzenes and bibenzyls.[7] Thus the first step is electron transfer from the benzylic donor to singlet excited NDN. Accordingly, only donors that quench the NDN fluorescence react, and the reaction does not take place in apolar solvents. Furthermore, the value of K' (ratio between the intercept at the origin and the slope in the Φ^{-1} vs [donor]$^{-1}$ plot) is near to that of K_{sv} obtained from fluorescence measurements (Table II).

The present survey shows that a further condition needs to be met for the occurring of the reaction, viz. that an exothermic pathway is available for the fragmentation of the donor radical cation (eq 6 and/or 7). Considerable effort has been recently devoted to the determination of the thermodynamics of radical ions reactions.[12] In the meantime, direct measurements have made available the oxidation potential of several benzyl radicals in acetonitrile,[13] and these values can be used, in conjunction with the arene oxidation potentials and bond-dissociation energies, for determining the ΔH of radical-cation fragmentation (e.g. eq 6, 7) through thermochemical cycles.[13] Through this approach,[14] proton loss is calculated to be the preferred pathway from the diphenylmethane radical cation (**1a**$^{\bullet+}$) (eq 8), while cleavage to give a hydrogen atom and the benzhydryl cation (eq 9) is endothermic. Likewise, it can be determined[14] that the bibenzyl radical cation undergoes deprotonation (eq 10) rather than carbon–carbon cleavage (eq 11) in accordance with experiments.[7b] On the other

$$\mathrm{PhCHRX^{\bullet+} \rightarrow PhCRX^{\bullet} + H^{+}\ or\ PhCRX^{+} + H^{\bullet}} \quad (6)$$

$$\mathrm{PhCHRX^{\bullet+} \rightarrow PhCHR^{\bullet} + X^{+}\ or\ PhCHR^{+} + X^{\bullet}} \quad (7)$$

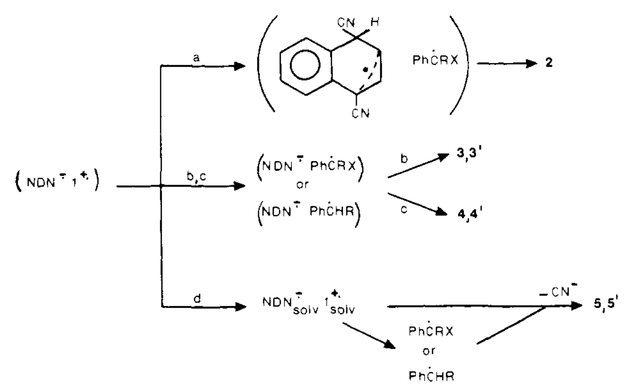
$$\mathrm{Ph_2CH_2^{\bullet+} \rightarrow Ph_2CH^{\bullet} + H^{+}} \qquad \Delta H = -29\ \mathrm{kcal\ M^{-1}} \quad (8)$$

$$\mathrm{Ph_2CH_2^{\bullet+} \rightarrow Ph_2CH^{+} + H^{\bullet}} \qquad \Delta H = 36\ \mathrm{kcal\ M^{-1}} \quad (9)$$

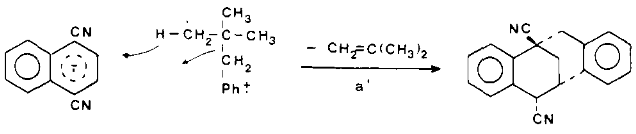
$$\mathrm{PhCH_2CH_2Ph^{\bullet+} \rightarrow Ph\dot{C}HCH_2Ph + H^{+}} \quad \Delta H = -21\ \mathrm{kcal\ M^{-1}} \quad (10)$$

$$\mathrm{PhCH_2CH_2Ph^{\bullet+} \rightarrow PhCH_2^{\bullet} + PhCH_2^{+}} \quad \Delta H = 24\ \mathrm{kcal\ M^{-1}} \quad (11)$$

Scheme III



Scheme IV



hand, in the case of 1,1,2,2-tetraphenylethane (**1c**)[14] carbon–carbon cleavage (eq 1) becomes exothermic (ΔH = -4 kcal M^{-1}), and indeed this is the main process observed in the photochemical reaction with NDN (see above).

While thermochemical considerations are obviously important, e.g. in rationalizing the efficient cleavage of the C–X bond in silane **1q** and stannane **1r** on the basis of their low bond-dissociation energy, a more detailed scheme is needed in order to adequately discuss the mechanism of the present reactions and the effect of substituents in the α position of the benzylic donors, since there are large variations both in the type of products formed and in the efficiency of the reaction, which are not satisfactorily explained on the basis of the oxidation potential of the donor and the exothermicity of the radical cation cleavage alone (e.g. adducts of type **3** with Ph_2CH_2 but essentially reduction to $NDNH_2$ with Ph_2CHOH and scarce reactivity with Ph_2CHOMe and Ph_2CHSMe; products of type **2** and **5** with $PhCH_2CMe_3$ but of type **4** with $PhCH_2CH_2CH{=}CH_2$). Our mechanistic proposal as depicted in Scheme III envisages different reaction paths and results from the development of a previous proposal.[7]

Path a involves in cage proton transfer from $PhCHRX^{\bullet+}$ to $NDN^{\bullet-}$ and subsequent in cage addition of the neutral radicals to yield products of type **2**. We previously observed that this path predominates with methylbenzenes and explained the stereochemistry of the adducts on the basis of the stereoselectivity of the initial proton transfer.[7b] Within the present series of benzyl derivatives this reaction takes place with neopentylbenzene **1h** to yield **2h**, albeit in moderate yield, but not with benzhydryl derivatives or when the group X^+ is detached in preference to a proton. The second observation is obvious, since path a requires that a proton is transferred first, the first one points to a sterical hindering by a phenyl (and to a lesser degree by a *tert*-butyl) group on this reaction (see also below).

In an apparent exception, a product of type **2** is formed via splitting of the X^+ group, not of the proton. This is the case with **2'h** ≡ **2** from **1h**. The reaction is thermodynamically affordable (ΔH for carbon–carbon cleavage in the neopentylbenzene radical cation is ca. 0 kcal M^{-1} [14]), and Scheme IV shows that a variation of the previous pathway (path a') is possible in this case since the proton is indirectly transferred to $NDN^{\bullet-}$ from the isopropyl cation. We had previously observed a similar reaction with $PhCMe_2CMe_2H$.[7c]

Paths b and c involve formation of a benzyl radical either by proton transfer to the medium or by loss of the cation X^+, addition between the neutral benzylic radical and $NDN^{\bullet-}$ in either position 2 (path b) or position 1 (path c), and final reprotonation. Accordingly, the same product (**3a**) is obtained from diphenylmethane (via deprotonation) and from tetraphenylethane (via carbon–carbon cleavage), and again the same product is obtained both

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(14) Values used for the present calculations are as follows: bond-dissociation energies, Ph_2CH-H, 77 kcal M^{-1}; $PhCH_2$-Ch_2Ph, 62.3 kcal M^{-1}; Ph_2CH-$CHPh_2$, 38 kcal M^{-1}; oxidation potentials of the hydrocarbons, Ph_2CH_2, 2.25 V vs SCE; $PhCH_2CH_2PH$, 2.4 V; $Ph_2CHCHPh_2$, 2.15 V; $PhCH_2CMe_3$, taken as ca. 2.4 V; oxidation potentials of the radicals, $PhCH_2^{\bullet}$, 0.73 V vs SCE; $Ph_2CH^{\bullet}$, 0.35 V; $Me_3C^{\bullet}$, 0.09 V. See Weast, R. C., Ed. CRC Handbook of Chemistry and Physics; CRC Press; Boca Raton, 1986 and ref 8a and 13 and references cited therein. For experimental work on benzylic radical cation fragmentation under different conditions, see e.g.: Camaioni, D. M.; Franz, J. A. *J. Org. Chem.* **1984**, *49*, 1607.

from $PhCMe_2H$ and from $PhCMe_2CMe_2Ph$. That paths b and c and not path a are followed when loss of X^+ is easy ($X = SiMe_3$, $SnBu_3$, $CHPh_2$) requires no comment. As for the cases involving cleavage of a C–H bond, the present data show that preference for proton transfer to the medium rather than to $NDN^{\bullet-}$, i.e. paths b, c rather than path a, is related to the stability and bulkiness of the benzyl radicals. Path a requires that the radical ions approach very closely and takes place when both R and X are H or alkyl, whereas with diphenylmethane (**1b**), the second phenyl group hinders close approach and stabilizes the neutral radical. The two factors act in the same direction and the proton is transferred at an earlier stage, viz. at a larger donor–acceptor distance, and to the medium, not to the acceptor. The same holds for the heteroatom-stabilized radicals in the case of donors **1l**, **1o**, and **1p**. With **1f**, participation of the double bond to donation makes attainment of the conformation suitable for path a again difficult. The competition between attack of the radical to position 2 (path b leading to products **3** or **3′**) or to position 1 (path c leading to **4** or **4′**) cannot be rationalized without a detailed knowledge of the structure of the initial donor–acceptor complex, or of the following radical anion-radical complex. However, it is safe to assume that the polarization of the donor determines the conformation of such complexes, and the product distribution shows that it is actually so. Indeed, the attack is predominantly in position 2 when the aromatic donor is an hydrocarbon and in position 1 with benzylic ethers and thioethers, where the heteroatom certainly influences the conformation, but it is in position 2 with the alcohol **1l**, where the hydrogen bond again changes the structure. Remarkably, both modes of addition are observed with the organometallic derivatives **1q** and **1r**, probably because cleavage is so fast in these cases that there is no influence of the orientation of the initial complex on the efficiency of the reaction.

Some other observations about these pathways are in order. Thus, strongly stabilized radicals, such as $Ph_2CH^\bullet$, may in part diffuse prior to addition, and this is probably why with **1a** some trans adduct (product **6**) is formed along with the predominant in-cage product (*cis*-**3a**). Furthermore, splitting off of the X^+ group does not invariably lead to products **3** and **4**. Thus donors such as **1c–e** are cleaved, as it has been shown under different conditions,[9,10] but do not yield definite products with NDN. Apparently, the other groups present in these donors (cyclopropane ring, double bond, ether oxygen) localize the charge and thus favor separation of the radical ions and eventual cleavage of the free solvated radical cation rather than reactions originating from the radical ion pair.

In other cases, diffusion of the radical ions favored by localization of the charge on the heteroatom is a source of inefficiency (compare the low quantum yield with benzylic ethers and thioether), since no easy fragmentation is available and the fate of the solvated radical ion is back-electron transfer.

Finally, formation of products **3** and **4** requires reprotonation of the intermediate anions **9** and **10** by water present in the solvent (the fact that this is the last step determines the cis configuration of products **3**[7b]). An alternative path for the anions is loss of the cyanide anion to yield rearomatized naphthalenes (path d). We observe some 4-benzyl-1-naphthalenecarbonitriles, arising from attack to position 1 (path c′), viz. **5h** and **5** from neopentylbenzene and **5** as the main product from the stannane **1r**. Previously, we obtained in low yield products of this type from some hydrocarbon donors. Compounds of type **5** are not secondary products, and are not formed from the dihydro derivatives **4** during irradiation or workup in our case. Other workers carried out related reactions under basic conditions[11b–d] and obtained products of type **5** as well as 3-benzyl-1-naphthalenecarbonitriles. In that case, these obviously result from hydrogen cyanide elimination from products of type **4** and **3**, respectively.

Besides the donor–acceptor addition processes outlined in Scheme III, other reactions can be important. Thus, with some donors the main process involves formation of stable radicals and their diffusion and disproportionation to yield $NDNH_2$ and oxidation products from the donors. This is a quite ubiquitous (observed with **1a,f,l,m,n,o**) but unefficient process, except than with the alcohols **1l** and **1m** and with phenylbutene (**1f**). In the last case, predominance of product **7** is reasonably due to hydrogen transfer between the neutral radicals (eq 12).

$$\mathrm{NDNH^\bullet + Ph\dot{C}HCH_2CH{=}CH_2 \rightarrow NDNH_2\ (7) + PhCH{=}CHCH{=}CH_2} \qquad (12)$$

Table III. Effect of Deuteration on the Reaction of Benzhydrol

substrate	product (% yield)	$\Phi_{\lim}$	K', M^{-1}	% deuteration in compd **7** at C-1	at C-2
Ph_2CHOH	**3c** (14), **7** (28)	0.26	48		
Ph_2CHOD	**3e** (15), **7** (30)	0.28	45	55	24
Ph_2CDOH	**7** (30)	0.18	62	5	5

With the alcohols and particularly with benzhydrol (**1l**), the total quantum yield is relatively high ($\Phi_{\lim} = 0.26$) and there is indication that a different mechanism is operating. The deuteration pattern is revealing. Thus, the reaction with Ph_2CHOD leads to product **7** deuterated in position 1 and to a minor extent in position 2. It is apparent that the proton transferred to $NDN^{\bullet-}$ is the O–H rather than the C–H proton, in agreement with the idea that, although the bond-dissociation energy for the C–H bond is lower, deprotonation from the radical cation involves preferentially the polarized O–H bond. The final products then arise from the naphthyl radical by hydrogen transfer within the cage, disproportionation, or hydrogen abstraction from benzhydrol.

$$\mathrm{(NDNH^\bullet Ph_2CHO^\bullet) \rightarrow NDNH_2 + Ph_2CO} \qquad (13)$$

$$\mathrm{2NDNH^\bullet \rightarrow NDNH_2 + NDN} \qquad (14)$$

$$\mathrm{NDNH^\bullet + Ph_2CHOH \rightarrow NDNH_2 + Ph_2\dot{C}OH} \qquad (15)$$

With Ph_2CDOH very little deuteration results in product **7**. Other differences are that no adduct **3l** is formed and quantum yield is lower (Table III). These results are easily rationalized considering the deuterium effect on reactions such as eq 13 and 15 and in the formation of product **3l**, all of which require abstraction from the C–H group. Thus with **1l**-*C-d* disproportionation remains the only pathway available for reduction of $NDNH^\bullet$ to $NDNH_2$, and the quantum yield decreases. We[7b] and previously other groups[15a] already reported examples of deuterium effect on proton transfer from the radical cations of alkyl aromatics.

Furthermore, with **1l** the value of K' obtained from linear interpolation of the Φ^{-1} vs $[\text{donor}]^{-1}$ plot is clearly too high to be considered in accordance with the value obtained from fluorescence quenching. This lower than expected reaction quantum yield at high donor concentration is probably related to an unproductive quenching of the radical ion pair by the donor:

$$\mathrm{(NDN^{\bullet-}Ph_2CHOH^{\bullet+}) + Ph_2CHOH \rightarrow NDN + 2Ph_2CHOH} \qquad (16)$$

We previously observed[7] that protic additives (e.g. MeOH or H_2O) decrease the quantum yield of related reactions at similar concentrations (ca. 10^{-2} M), probably because formation of a hydrogen bond stabilizes the radical ion pair and results in increased back-electron transfer vs chemical reaction. The alcohols **1l** and **1n** act through a similar mechanism, and K' results are high (Tables II and III).

In conclusion the easy formation of benzylic radical cations by electron transfer to singlet excited NDN affords a way to study the competition between the different fragmentation pathways available to such species since different chemical products are formed. Back-electron transfer is fast under these conditions, probably around 5×10^9 M^{-1} s^{-1}.[15b] This work shows that besides C–H bonds (as with **1a**) also C–C (**1b**), C–Si (**1q**), C–Sn (**1r**), and O–H (**1l**) bonds cleave within this time scale when the process is thermodynamically allowed. The limiting quantum yield never

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exceeds 0.3, showing that the cleavage is never faster than back-electron transfer. On the other hand, despite the acidity of benzylic radical cations (pK_a −9 to −13 for toluene),[12] proton transfer may be slow. Indeed proton transfer to the medium from $PhCHRX^{\bullet +}$ (R, X = H, alkyl) is inefficient (quantum yields for paths b and c $\leqslant 0.01$),[4,7b,c] while proton transfer within the close contact radical ion pair (path a) may be much faster (quantum yield up to 0.3 with cumene).[7c] Added stabilization makes deprotonation according to path b more efficient, e.g. $\Phi = 0.15$ in the case of Ph_2CH_2, and of course, paths b and c are efficient when there is a weak bond, as in the organometallic derivatives **1q** and **1r**. Since the role of radical cations in chemistry is probably more important than hitherto recognized, these results could help in predicting new reactions, together with the physical data about such species that are becoming available. On the other hand, new stereospecific photoaddition reactions have been uncovered (e.g. those yielding products **2** and **3**) and the conditions for their occurring have been determined.

Experimental Section

1,4-Naphthalenedicarbonitrile was prepared and purified as previously described. Spectrograde acetonitrile (Carlo Erba) was used as obtained or was dried by refluxing over CaH_2 for the experiments with deuterated substrates. Diphenylmethane (**1a**), phenylcyclopropane (**1e**), allylbenzene (**1g**), benzyl alcohol (**1h**), and benzyltrimethylsilane (**1q**) were commercial products and were purified by fractional distillation or recrystallization.

1,1,2,2-Tetraphenylethane (**1b**) was prepared from benzhydrylmagnesium chloride;[16] 2,2-diphenylethyl methyl ether (**1c**) was prepared from diphenylmethylpotassium and chloromethyl methyl ether,[17] 2-phenylethyl methyl ether (**1d**) was prepared from phenylmagnesium chloride and chloromethyl methyl ether,[18] 4-phenylbut-1-ene (**1f**) was prepared from benzylmagnesium chloride and allyl bromide,[19] neopentylbenzene (**1h**) was prepared from benzylmagnesium chloride and *tert*-butyl chloride,[20] benzhydryl chloride (**1i**) was prepared from the alcohol, methyl diphenylacetate (**1j**) was prepared from the acid, diphenylacetonitrile (**1k**) was prepared from phenylacetonitrile,[21] benzhydrol (**1l**) was prepared from benzophenone, benzhydryl methyl ether (**1m**) was prepared from the bromide and sodium methylate, benzyl methyl ether (**1n**) was prepared from the bromide and sodium methylate, benzyl methyl thioether (**1q**) was prepared from the thiol and dimethyl sulfate,[22] and benzyltri-*n*-butylstannane (**1r**) was prepared from chlorotri-*n*-butylstannane.[23] Benzhydrol-*C-d* was prepared from $LiAlD_4$ reduction of benzophenone, and benzhydrol-*O-d* was prepared from repeated shaking of a benzhydrol solution with D_2O. In both cases, spectroscopic analysis showed less than 2% of undeuterated compound.

Preparative Photochemical Reactions. An acetonitrile solution (140 mL) containing 200 mg (1.12 mM) of NDN and 500 mg (3 mM) of diphenylmethane (**1a**) was refluxed, cooled while flushing with pure Ar, and irradiated with a Pyrex-filtered 150-W Helios Italquartz medium-pressure mercury arc at 17 °C until NDN was almost completely converted (10 h, TLC). The solution was examined by VPC and the presence of 1,1,2,2-tetraphenylethane (7 mg, 1.5% of starting **1a**) and benzophenone (16 mg, 3%) was ascertained. The solvent was evaporated and the raw photolysate was chromatographed on silica gel, eluted with cyclohexane in order to eliminate excess **1a** and then with cyclohexane–EtOAc mixtures. The following products were obtained, besides unreacted NDN (8 mg): *trans*-2-(1,1-diphenylmethyl)-1,2-dihydro-1,4-naphthalenedicarbonitrile (**6**), 41 mg (11%); the corresponding cis derivative **3a**, 168 mg (45%); 1,2-dihydro-1,4-naphthalenedicarbonitrile, 3 mg (1.5%).

Product **3a** (previously isolated from the reaction of NDN with **1b**): colorless needles, mp 171–2 °C (from benzene–cyclohexane); NMR (C_6D_6) δ 6.3 (d, J = 2.5 Hz, 3-H), 3.3 (d, J = 5.5 Hz, 1-H), 2.95 (dddd, 2-H), 4.2 (d, J = 12 Hz, Ph_2CH), in $CDCl_3$ 1-H, 2-H, and the benzylic H appear at δ 3.6, 4.35, and 3.65, respectively.

Product **6**: colorless needles, mp 190 °C (from ligroin); NMR ($CDCl_3$) δ 7 (d, J = 2 Hz, 3-H), 3.97 (d, J = 1.5 Hz, 1-H), 3.3 (dddd, 2-H), 4.1 (d, J = 12, Ph_2CH). Besides the different values of the $J_{1,2}$ coupling constants (compare ref 24 for an analogous case), identification of compound **6** as the stereoisomer of **3a** is supported by the strong peak at m/z 319 ($M^+ - HCN$) in the mass spectrum of the first and at 344 m/z ($M^+ - H_2$) in the spectrum of the latter compound.

The reaction with the other donors was carried out analogously with the results reported in Table I. Some of adducts obtained (**2–4**, **4o**, **5**, **7**) were identical (melting point, spectroscopic properties) with products previously obtained from the reaction with other benzyl derivatives[7] and other products were identified by comparison with authentic samples (e.g. $PhCH(SCH_3)CHPhSCH_3$, two diastereoisomers).

New compounds gave correct analytic data and the structures were assigned on the basis of their analytic and spectroscopic properties, after comparison with previously obtained derivatives of similar structure.[7] General diagnostic properties are as follows. One or two CN absorptions at 2240–2215 cm^{-1} in the IR spectrum; the UV spectra for the naphthalenes **5** gave a vibrationally resolved band with maximum at ca. 300 nm (log ϵ 4.1); those for the 1,2-dihydronaphthalenes **3** and **4** gave a maximum at 272–279 nm (log ϵ 3.5), and those for the tetracyclic derivatives **2** have maximum at ca. 270 nm (log ϵ 2.6); mass spectra fragmentation patterns are in accordance with the proposed structure. The most relevant characteristics are as follows.

From the reaction with **1f**, *trans*-1-(1-phenylbut-3-enyl)-1,2-dihydro-1,4-naphthalenedicarbonitrile (**4f**): mp 45 °C (from cyclohexane); NMR ($CDCl_3$) δ 6.65 (dd, J = 3, 6 Hz, 3-H), 2.5–2.8 (AB part of ABX system, H-2), 4.8 (d), 4.65 (d), 5.1 (m, vinyl), 2.3 (m), 2.9 (d, $CHCH_2$). Azetine **8**: mp 110 °C dec (rechromatographed on silica gel with benzene); NMR ($CDCl_3$) δ 3.75 (dd), 3.6 (dd), and 3.2 (m) (azetine protons), 2.8 (t), 2.05 (m, CH_2CH_2).

From the reaction with **1h**, 12-(1,1-dimethylethyl)-6,11-dicyano-5,11-methanodibenzo[*a*,*e*]cyclooctene (**2h**): oil (from chromatography); NMR ($CDCl_3$) δ 4.45 (d, J = 3.5 Hz, 6-H), 3.75 (ddd, 5-H), 3.3 (dd, J = 1, 14 Hz) and 2.35 (dd, J = 5, 14 Hz) (CH_2), 3.05 (s, 12-H), 1.15 (s, *t*-Bu). 4-(2,2-Dimethyl-2-phenylpropyl)-4-naphthalenecarbonitrile (**5h**): colorless, fluorescent oil (from chromatography); NMR ($CDCl_3$) δ 4.8 (s, CH), 0.9 (s, *t*-Bu).

From the reaction with **1l**, product **3l**: colorless needles, mp 227–8 °C (from benzene); NMR ($CDCl_3$) δ 6.2 (d, J = 2.5 Hz, H-3), 4.55 (dd, H-2), 3.9 (d, J = 9.5 Hz, H-1). A further adduct of unrecognized structure was obtained in 10% yield as a crystalline material; mp 246 °C (from methanol); NMR δ 9.25 (dd), 8.5 (dd), 7.3–7.5 (m); IR (KBr) 2220, 1760, 1665 cm^{-1}.

From the reaction with **1p**, both diastereoisomers of product **4p** were found in approximately equal amounts and we did not succeed in obtaining pure samples but only fractions ca. 80% pure in each isomer. The first eluting (cyclohexane–ethyl acetate 9–1) isomer: NMR ($CDCl_3$) δ 6.9 (dd, J = 3, 7 Hz, 3-H), 3.8 (dd) and 3.05 (dd) (CH_2, J_{gem} = 19 Hz), 3.9 (s, PhCH), 1.9 (s, SMe). The latter one: NMR ($CDCl_3$) δ 6.6 (dd, J = 3, 6 Hz, 3-H), 2.8 (AB system, CH_2), 3.85 (s, PhCH), 1.6 (s, SMe).

Quantitative Measurements. Fluorescence spectra were measured by means of an Aminco-Bowman MPF spectrophotometer. Fluorescence intensities and photochemical quantum yields were measured in 1-cm optical path cells after deoxygenation by means of four freeze–degas–thaw cycles. The photochemical reaction was effected with 313-nm radiation obtained from a focalized Osram 200 W high-pressure mercury arc by means of an interference filter ($\Delta\lambda_{1/2}$ = 5 nm), flux ca. 1×10^{-7} einstein min^{-1} cm^{-2}.

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