under 4 atm of hydrogen overnight. After filtering through Celite, the filtrate was washed (2 M HCl, 2 × 50 mL), dried ($MgSO_4$), and evaporated down to give **22** as a yellow oil, which was further purified by a SiO_2 column with $CH_2Cl_2/CHCl_3$ (1:1).

An alternate reductive cyclization step was to add a 20% titanium(III) chloride HCl solution and twice that volume of ammonium acetate (4 M) to the crude nitrostyrene in a minimum volume of acetone. After 10 min at room temperature, extraction (ether) and purification as above gave **22** as a yellow oil: UV λ_{max} (MeOH) 220 nm (log ϵ 4.3), 270 (3.5), 295 (3.5); IR (KBr) 3410–3430, 1624, 1574, 1507, 1149, 908, 836, 759, and 716 cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 3.75 (s, 3 H), 6.30 (t, 1 H, $J_{H_2H_3}$ = 2.6 Hz), 6.74 (d, 1 H, J = 1.9 Hz), 6.89 (d, 1 H, J = 1.9 Hz), and 11.2 (br, 1 H). Yields varied between 40% and 60%.

Acknowledgment. This invesgitation was financially supported by the National Institutes of Health (Grants GM 09863 and 1-P01-CA26731-04), the National Research Service Award T32-CA09112, and the US Army contract 9283DAMD 17-82-C-2235.

Photochemical Reaction of 1,4-Naphthalenedicarbonitrile with Alkylbenzenes and Bibenzyls

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Abstract: The photochemical reaction of 1,4-naphthalenedicarbonitrile with some alkylbenzenes and bibenzyls has been examined. A unitary mechanistic picture is formulated on the basis of product study, deuteration experiments, and fluorescence and reaction quantum yield measurements. Proton transfer within the singlet radical ion pair followed by in-cage cycloaddition of the two radicals yields stereoselectively 5,11-methanodibenzo[*a,e*]cyclooctene derivatives (**8**). Reaction of benzyl radicals (formed by protolysis or, for radical cations having no benzylic proton, by C–C bond cleavage) with unprotonated $NDN^{\bullet-}$ leads, again stereoselectively, to 2-benzyl-1,2-dihydronaphthalenes (**9**). Escape of the donor radical cation and following C–H or C–C bond cleavage leads to a different product; thus, benzyl radicals are trapped by NDN to yield substitution products (**11**) or recombine. Benzyl cations are trapped by nucleophiles.

The synthetic usefulness of photochemical electron transfer is demonstrated by the number and variety of the applications reported in the last decade.[1] As it has been recognized by Arnold in his pioneering studies,[2] this process requires that electron transfer (e.g., eq 1 for the case of a singlet excited acceptor, A, and a benzene derivative, PhX, as the donor) be exothermic.[3]

$$A^{1*} + PhX \rightarrow A^{\bullet-} + PhX^{\bullet+} \qquad (1)$$

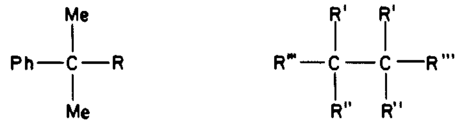
Whether this condition is met is easily ascertained on the basis of the redox potentials of the two compounds and of the excitation energy of A (Weller equation[4]). Of course, the efficiency of the ensuing chemical reaction is not as easily predicted, the only possible generalization being that back electron transfer with or without energy dissipation (eq 2) is the fate of the pair of radical

$$A^{\bullet-} + PhX^{\bullet+} \rightarrow A^* + PhX \qquad (2)$$

$$A^{\bullet-} + PhX^{\bullet+} \rightarrow A + PhX$$

ions of opposite sign, unless some fast process, e.g., a molecular vibration,[5] starts a concurrent pathway, leading to chemical transformation. This explains why reactions involving radical ions of aromatic olefins (X = >C=C<) form by far the larger class of reactions within electron-transfer photochemistry of benzene derivatives (compare ref 6), since in this case deformation of the carbon–carbon bond opens exactly such a pathway.

Chart I. Organic Substrates under Study



1, R = H
1', R = D
2, R = Me
3, R = $CHMe_2$

4, R' = H, R'' = Ph, R''' = H
5, R' = Me, R'' = Ph, R''' = Me
6, R' = H, R'' = H, R''' = C_6H_4-*p*-OMe
7, R' = Ph, R'' = Ph, R''' = H

Conceivably, another fast process initiating a chemical reaction is proton transfer, e.g., from the radical cation of an alkylbenzene. Indeed, thermochemical calculations show that the toluene radical cation has a pK_a value of ca. −10,[7] and we reported a photochemical reaction between 1,4-naphthalenedicarbonitrile (NDN) and toluene and other methylbenzenes.[8] This intriguing reaction (the main product is a bicyclo[3.3.1]nonane derivative) involves electron transfer followed by base-mediated proton transfer within the geminate radical ion pairs and stereoselective addition between naphthyl and benzyl radicals before they diffuse apart.[9]

A partial mechanistic analogy to the above reaction can be found in the NDN-sensitized photooxygenation of bibenzyl derivatives, recently reported by Griffin and Das,[10,11] in that benzyl

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(1) Some leading references are the following: (a) Arnold, D. R.; Wong, P. C.; Maroulis, A. J.; Cameron, T. S. *Pure Appl. Chem.* **1980**, *52*, 2609. (b) Mattes, S. L.; Farid, S. *Acc. Chem. Res.* **1982**, *15*, 80. (c) Caldwell, R. A.; Creed, D. *Acc. Chem. Res.* **1980**, *13*, 45. (d) Albini, A. *Synthesis* **1981**, 249. (e) Yang, N. C.; Yates, R. L.; Masnovi, J.; Shold, D. M.; Chiang, W. *Pure Appl. Chem.* **1979**, *51*, 173. (f) Davis, H. F.; Das, P. K.; Griffin, G. W.; Timpa, J. D. *J. Org. Chem.* **1983**, *48*, 5256.

(2) Arnold, D. R.; Maroulis, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 5931.

(3) However, in certain cases an *endothermic* electron transfer is involved in an efficient photoreaction. See, e.g.: Schaap, A. P.; Lopez, L.; Gagnon, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 663. See also ref 6.

(4) (a) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259. (b) Weller, A. *Nobel Symp.* **1967**, *5*, 413. (c) Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 834.

(5) Other mechanisms increasing the efficiency of an overall process initiated by photochemical electron transfer, such as secondary electron transfer or chain mechanisms, have been discussed in detail by Farid; see ref 6.

(6) Mattes, S. L.; S. Farid, S. *Org. Photochem.* **1983**, *6*, 223.

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

(8) Albini, A.; Fasani, E.; Oberti, R. *Tetrahedron* **1982**, *38*, 1027.

(9) Albini, A.; Fasani, E.; Sulpizio, A. *J. Am. Chem. Soc.* **1984**, *106*, 3562.

(10) Reichel, L. W.; Griffin, G. W.; Muller, A. J.; Das, P. K.; Ege, S. *Can. J. Chem.* **1984**, *62*, 424.

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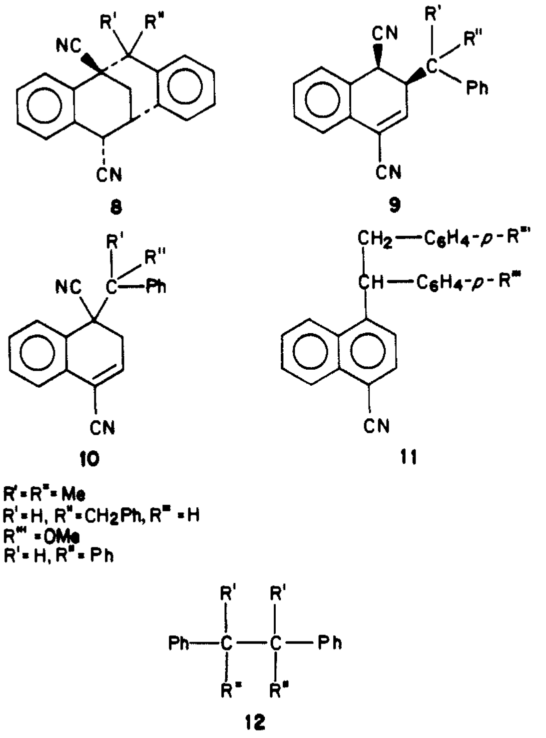
Chart II. Products from the Irradiation of NDN in the Presence of Substrates 1–7



radicals are formed by electron transfer followed by C–C bond cleavage.

Comparison between this work and our own suggests some questions. Do bibenzyl radical cations undergo only C–C and no C–H bond cleavage? The first process yields the same benzyl radicals which can be obtained from the appropriate alkylbenzene by C–H bond cleavage. Das and Griffin report the reaction of these radicals with oxygen, but our previous experience suggests that, in deoxygenated solution, reaction with NDN or NDN$^{\bullet-}$ should be observed. It was hoped that the study of the photochemical reaction between NDN and some alkylbenzenes and bibenzyls, potentially giving rise to the same intermediates, would help in understanding the chemistry of benzyl radical cations and radicals formed by electron transfer and in better defining the mechanism and the scope of this multistep reaction.

Results

Preparative Irradiation. In pursuance of our work we now report the photochemical reaction between NDN and some branched-chain alkylbenzenes as well as some bibenzyls. The donors used in this work are shown in Chart I, and the products obtained by photochemical reaction with NDN are shown in Chart II.

A first group of donors was selected with the aim of establishing that protolysis from the radical cation occurs exclusively from the benzylic position. Thus, isopropylbenzene (**1**) quenches the fluorescence of NDN almost as rapidly as toluene. As in the case of the latter, exciplex emission and no photochemical reaction are observed in apolar solvents, whereas in acetonitrile no exciplex emission appears and a reaction takes place. The situation remains the same for all the donors considered in the present work, no reaction being observed when the solvent is cyclohexane or benzene. Unless otherwise stated, the reactions reported in the following were carried out in wet (0.1% water content) acetonitrile.

Under this condition, two products were isolated from the photochemical reaction of NDN with **1**, and their structure was determined on the basis of their spectroscopic and analytic properties (Tables I and II). These compounds are the analogues of two out of three products obtained in the corresponding reaction of NDN with toluene. They are 6,11-dicyano-12,12-dimethyl-5,11-methano-5,6,11,12-tetrahydrodibenzo[*a*,*e*]cyclooctene (**8a**) and *cis*-2-(1,1-dimethylbenzyl)-1,2-dihydro-1,4-naphthalenedicarbonitrile (**9a**), whereas in contrast to the reaction of toluene, no product arising from the substitution of a cyano with a benzyl group is obtained with **1**. The main product has in both cases the tetracylic structure of type **8**. Clearly no hydrogen abstraction from the β position is taking place. This, by the way, further confirms that the process consists of electron transfer followed by proton transfer, rather than direct hydrogen abstraction.[12]

Table I. Percent Product Yield from the Irradiation of NDN in Acetonitrile[a]

no.	donor	products (% yield)
1	**1**, 0.3 M	**8a** (45), **9a** (10)
2	**2**, 0.3 M	none
3	**3**, 0.2 M	**8a** (33), **10a** (8)
4	**4**, 0.2 M	**8b** (40), **9b** (33), **10b** (22), **11b** (2), **12b**
5	**5**, 0.06 M	**9a** (60)
6	**6**, 0.06 M	**11c** (45)
7	**7**, 0.05 M	**9d** (57), Ph_2CO, **13** (65),[b] Ph_2CH_2, **14** (40)[b]
8	**7**, 0.05 M[c]	**9d** (58)
9	**7**, 0.05 M[d]	**9d** (42), **10d** (4), **14** (220),[b] Ph_2CHOMe, **15** (20)[b]

[a] Containing 0.1% water, unless otherwise stated. [b] Moles of the product for mole of reacted NDN. [c] In anhydrous acetonitrile. [d] In acetonitrile containing 1% methanol.

Table II. Relevant Characteristics of New Products[a]

		selected ^1H NMR values			
				5,11-CH_2	
prod	mp, °C	5-H	6-H	exo	endo
8a	202–203[b]	4.5	3.6	3.05	2.4[g]
8b	171–172[b]	2.6	3.5	1.95	1.85[h]
		1-H	2-H	3-H	
9a	175–177[c]	3.6	3.05	6.85[g]	
9b	154–155[d]	3.85	2.9	6.5[g]	
9d	171–172[c]	3.3	2.95	6.3[h]	
10a	160[c]		3.05	6.2[g]	
10b	oil		3.0	6.9[g]	
10d	86–88[c]		2.95	6.6[g]	
		H_α	H_β		
11b	125[c]	5 t	2.9 t[g]		
11c	210[c,f]	4.3 t	2.85 d[g]		

[a] Further diagnostic properties are as follows. One or two CN absorptions at 2240–2215 cm^{-1} in the IR spectrum, UV spectra: for the naphthalenes **11** a vibrationally resolved band with maximum at ca. 300 nm (log ϵ 4.1); for the 1,2-dihydronaphthalenes **9** and **10** maximum at 272–279 nm (log ϵ 3.5); for the tetracyclic derivatives **8** maximum at ca. 270 nm (log ϵ 2.6). Mass spectra fragmentation patterns are in accord with the proposed structure. [b] Recrystallization from toluene. [c] From benzene–cyclohexane. [d] From benzene. [e] From cyclohexane. [f] Sublimation point in closed capillary. [g] In $CDCl_3$. [h] In C_6D_6.

With *tert*-butylbenzene (**2**), quenching of NDN fluorescence is still effective (the rate is two-fifths of that of toluene), but no photochemical reaction is observed, showing again that the presence of a benzylic proton is a prerequisite.

In contrast, (1,1,2-trimethylpropyl)benzene (**3**), a somewhat less effective quencher of NDN fluorescence due to the increased steric hindering (k_q is ca. one-fourth of that of toluene), does react while having no benzylic proton. Two products are obtained, the main one being identical with the tetracyclic derivative **8a** obtained from isopropylbenzene and the minor one being identified as 1-(1,1-dimethylbenzyl)-1,2-dihydro-1,4-naphthalenedicarbonitrile (**10a**). Apparently in this case the donor undergoes C–C bond cleavage, so that products containing the dimethylbenzyl group are obtained from **3** just as from **1** and the product distribution

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(11) Davis, H. F.; Das, P. K. Reichel, L. W.; Griffin, G. W. *J. Am. Chem. Soc.* **1984**, *106*, 6968.

(12) Radical abstraction from isopropylbenzene by Cl$^\bullet$ proceeds for ca. 90% from the α and 10% from the β positions: Kharash, M. S.; Brown, H. C. *J. Am. Chem. Soc.* **1939**, *61*, 2142. With *tert*-butoxy radicals reactivity at the β position is limited but detectable, e.g., 3% in the case of ethylbenzene. Furthermore some reaction with *tert*-butylbenzene is observed, although slower by a factor 10 with respect to toluene, Wagner, P.; Walling, C. *J. Am. Chem. Soc.* **1965**, *87*, 5179.

from both donors differs only insofar as the minor products are concerned.

Among the bibenzyls used in the present work, the parent molecule **4** was found to undergo exclusively C–H bond cleavage and to afford a product distribution closely analogous to that obtained with toluene and containing the 1,2-diphenylethyl radical. The main product is the tetracyclic derivative **8b**, accompanied by the dihydro adducts in position 2 (of cis stereochemistry, **9b**) and in position 1 (**10b**) as well as by traces of the naphthalene arising from substitution of the cyano group (**11b**) and a small amount of the radical coupling product, 1,2,3,4-tetraphenylbutane (meso + racemic forms, **12b**). No product arising from C–C cleavage, which would be identical with those obtained from toluene, was detected.

With the wholly methylated bibenzyl 2,3-dimethyl-2,3-diphenylbutane (**5**), protolysis is no more possible, but C–C bond cleavage is expected to be facile as it involves two benzylic and tertiary carbon atoms. This is indeed the case, but the course of the reaction turns out to be different, in that it leads exclusively to the cis adduct in position 2 (**9a**) and none of the other products containing the dimethylbenzyl group obtained from either **1** or **3**, in particular **8a**, which is the main product from both.

Substitution in the aromatic ring also has a profound effect on the photoreactivity of bibenzyl with NDN. Thus, 4,4′-dimethoxybibenzyl (**6**) is a much better quencher of NDN fluorescence than unsubstituted **4**, k_q now approaching the diffusion-controlled limit, but the photochemical reaction is much slower and its course different, the only process being now substitution of a cyano group by the radical formed by proton detachment, to form 4-[1,2-bis(4-methoxyphenyl)ethyl]-1-naphthalenecarbonitrile (**11c**).

Finally, the reactivity with 1,1,2,2-tetraphenylethane (**7**), an efficient quencher of NDN fluorescence, was examined. In this case, if the reaction is carried out, as in the previous cases, in acetonitrile containing 0.1% water, benzophenone (**13**) and diphenylmethane (**14**) are formed together with a single NDN-derived product, viz., the dihydro adduct bearing the benzydryl group in position 2 (cis configuration, **9d**). On the other hand, in anhydrous acetonitrile the adduct **9d** is formed in the same good yield as before, but products **13** and **14** are absent. Apparently, compound **7** undergoes C–C bond cleavage under this condition, and two independent processes follow, one leading to the adduct **9d**, the other, in the presence of water, to compounds **13** and **14**. In order to obtain more information about the latter process, the reaction of NDN with **7** was repeated in acetonitrile containing 1% methanol. Under this condition the yield of diphenylmethane is enhanced and some benzydryl methyl ether (**15**) is formed. As for the NDN-derived product, the yield is somewhat diminished and a minor amount of the 1-benzydryl dihydro adduct **10d** is also formed.

Quantitative Measurements. From the results reported above it is apparent that either the C–H or C–C bond is cleaved in the NDN-sensitized photoreaction of alkylbenzenes and bibenzyls, depending on their structure. The intermediates thus formed are trapped by NDN to yield substitution and addition derivatives in fair yield or, in the case of compound **7**, react with nucleophilic solvents where present.

In order to discuss the different reactions observed, it must first be demonstrated that the general mechanism remains the same throughout this series of reactions, viz., that in every case electron transfer from the donor to singlet excited NDN initiates the reaction. A first indication in this sense comes from the fact that photochemical reaction is observed only when the donor quenches the fluorescence of NDN (for donors **1**–**7** electron transfer to NDN is exothermic[13]) and only in polar medium. The fact that proton abstraction occurs exclusively from the benzylic position is also an indication, as mentioned above.

Table III. Fluorescence Quenching Constant and Reaction Quantum Yields[a]

donor	$k_{et}\tau$, M^{-1} [b]	$k_{et}\tau$, M^{-1} [c]	ϕ_r [d]	ϕ_{lim} [e]	$10^{-10}k_{et}$, M^{-1} s^{-1} [f]
PhMe	19	18.5	0.022	0.07	0.19
1	17	18.5	0.08	0.3	0.17
1′	17	18	0.08	0.29	0.17
2	7.5		10^{-4}		0.07
3	4.2		0.01		0.04
4	18.5	21.5	0.075	0.25	0.18
5	99		0.018		0.99
6	195		0.017		1.95
7	125	128	0.015	0.021	1.25

[a] In degassed acetonitrile. [b] Stern–Volmer constants from fluorescence quenching. [c] From the plot of reaction quantum yield vs. donor concentration, Figure 1. [d] At 0.02 M donor concentration. [e] At infinite donor concentration, Figure 1. [f] Taking τ_s = 10.0 ns, ref 2.

A quantitative description of the electron-transfer process is obtained from fluorescence quenching and reaction quantum yield measurements. If D is the donor and k_{et} is the rate constant for electron transfer to singlet excited NDN, the lifetime of which is τ, and the radical ions pair thus formed reacts to the observed products with the rate constant k_r or unproductively decays to the starting materials (k_d); the fluorescence quenching obeys the usual Stern–Volmer law

$$\frac{I_F{}^\circ}{I_F} = 1 + k_{et}\tau[D] \tag{3}$$

and the quantum yield for the reaction is

$$\Phi_r = \frac{k_r}{k_r + k_d}\,\frac{k_{et}[D]}{k_{et}[D] + 1/\tau} \tag{4}$$

or in the inverse form

$$\frac{1}{\Phi_r} = \frac{k_r + k_d}{k_r} = 1 + \frac{1}{k_{et}\tau[D]} \tag{5}$$

Thus, in the double-reciprocal plot of reaction quantum yield vs. donor concentration, a straight line is obtained, and the ratio intercept/slope corresponds to the same quantity $k_{et}\tau$ obtained from the Stern–Volmer fluorescence quenching analysis.

For the donors **1**–**7** linear plots were obtained for fluorescence quenching on the basis of the Stern–Volmer equation. The values obtained (Table III) vary over almost 2 orders of magnitude in the range 4.5–195 M^{-1}. As literature values of τ are 9.5–10 ns,[2,14a] this corresponds to a range of ca. 5×10^8 to 2×10^{10} M^{-1} s^{-1}, reaching the diffusion-controlled limit for the more electron-rich aromatics.[13a] The mechanism of NDN singlet quenching by alkylbenzenes and by bibenzyls is qualitatively different. Thus, in the first case the quenching constant correlates with the oxidation potential of the donor, determined by substitution on the aromatic ring (e.g., *p*-methoxytoluene > mesitylene > toluene), but bulky groups, such as a branched side chain, strongly limit the rate of the process (e.g., toluene ≃ isopropylbenzene (**1**) > **2** > **3**). In the latter case, substitution both at the benzylic position and at the aromatic ring increases the quenching constant (both **5** and **6** > **4**). This probably reflects participation of both aromatic rings of the bibenzyl to the electron-transfer process.[13b]

The quantum yield of reaction was measured at a donor concentration of 2×10^{-2} M and, for some representative donors, in the range of concentrations 5×10^{-3}–5×10^{-2} M. The expected linear dependence of $\Phi_r{}^{-1}$ vs. $[D]^{-1}$ is indeed observed (Figure 1), and the value of $k_{et}\tau$ obtained from this plot does not differ within experimental uncertainty from the value obtained from fluorescence measurements.

Deuteration Experiments. The above analysis suggests that electron transfer initiates the reaction. Proton transfer is obviously involved in the following steps, and deuteration experiments can be informative. We had previously compared perdeuterio- and

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(13) (a) For toluene ($E_{D/D^{\cdot+}}$ = 1.98 V vs. SCE), ΔG = −4.1 kcal M^{-1}, k_{et} = 1.9×10^9 M^{-1} s^{-1}, ref 9. At the other extreme, for 4,4′-dimethoxybibenzyl (**6**) ($E_{D/D^{\cdot+}}$ = 1.36: Becker, J. Y.; Miller, L. L.; Stermitz, F. R. *J. Electroanal. Chem.* **1976**, *68*, 181), ΔG = −18.4 kcal M^{-1}, k_{et} 1.95×10^{10} M^{-1} s^{-1}. (b) For examples of enhanced quenching by bichromophoric systems, see, e.g.: Lewis, F. D.; Correa, P. E. *J. Photochem.* **1983**, *21*, 87.

(14) (a) Das, P. K.; Muller, A. J.; Griffin, G. W. *J. Org. Chem.* **1984**, *49*, 1977. (b) Wagner, P. J.; Leavitt, R. A. *J. Am. Chem. Soc.* **1972**, *94*, 3669.

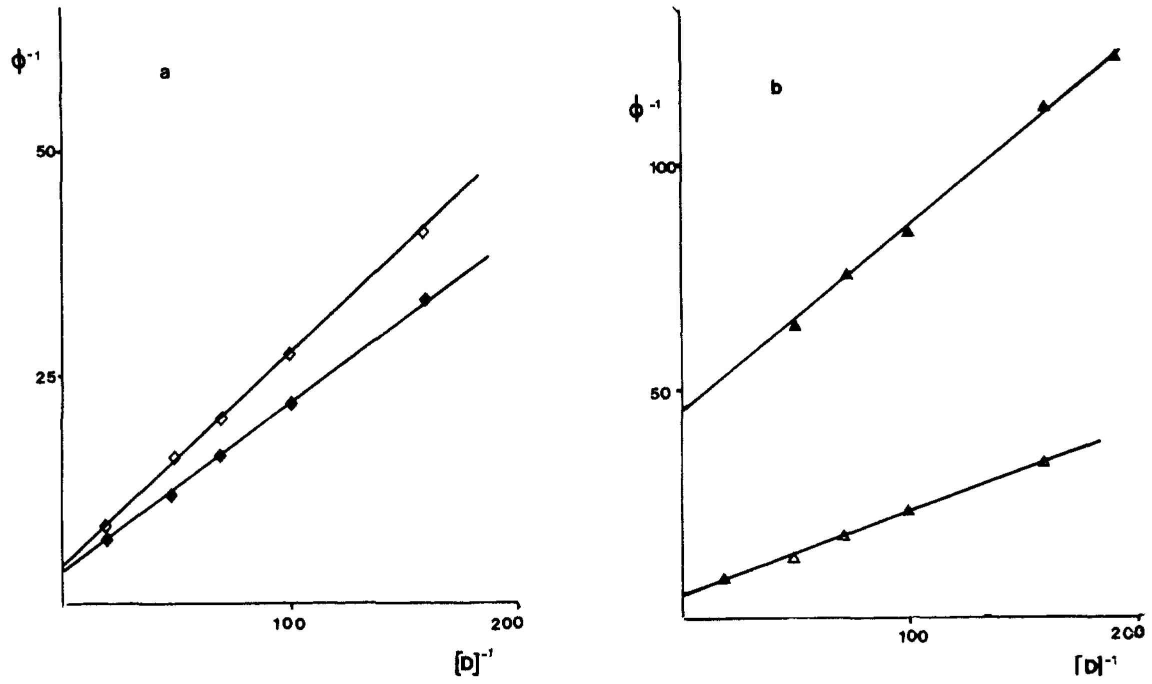


Figure 1. Double-reciprocal plot for the quantum yield of the photoreaction of NDN in the presence of isopropylbenzene, **1** (♦), isopropylbenzene-α-*d*, **1′** (◇), bibenzyl, **4** (△), and tetraphenylethane, **7** (▲).

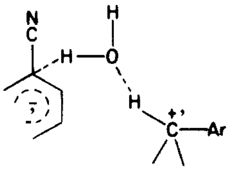
Table IV. Deuteration Experiments

donor	$k_r(H)/k_r(D)$	deuterium incorporation (%) product **8** α to CN	bridge	product **9** α to CN
A. Deuterium at the Benzylic Position in the Donor				
PhMe	3.9	0	0	0
1	1.15	20		10
B. Percent Deuterium Incorporation in the Presence of 0.1% D_2O				
PhMe		100	100	100
1		80	20	70
3		80	35	
4[a]		100	30	
7[a]				50

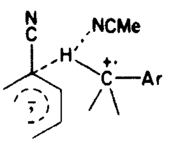
[a] With 1% D_2O.

perprotiotoluene,[9] showing that there is no change in k_{et} but a clear primary isotopic effect upon Φ_{lim}. Furthermore, proton transfer from the donor to $NDN^{\bullet-}$ (involving one proton in the case of product **9**, two protons in the case of product **8**) does not take place directly. In wet acetonitrile, water mediates proton exchange, so that deuterium labeling is lost starting from deuterated toluene, but deuterium is incorporated when perprotiotoluene reacts with NDN in the presence of traces of D_2O.

In the case of isopropylbenzene-α-*d* (**1′**), k_{et} is again unaffected, but there is no effect on Φ_{lim}. Furthermore some deuterium is retained in the products **8a** and **9a**, in both cases α to the cyano group (Table IV). Conversely, when perprotio **1** is reacted with NDN in the presence of 0.1% D_2O, deuterium incorporation is not complete. Apparently, proton transfer from the isopropylbenzene radical cation encounters a smaller barrier than from the toluene radical cation, perhaps due to the additional push toward the reaching of a planar configuration exerted by the methyl groups. Therefore, direct proton transfer to $NDN^{\bullet-}$ (**16**) is in this case possible, without requiring the intervention of a protic base (**17**).



16



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Comparison with an electron-transfer reaction occurring in the triplet state, viz., the photochemical reaction between trifluoroacetophenone and methylbenzenes, is useful. Also in that case k_{et} is not affected by deuteration. As for Φ_{lim}, the ratio $C_6H_5CH_3$ vs. $C_6H_5CD_3$ is 3.5 and $C_6H_5CMe_2H$ vs. $C_6H_5CMe_2D$ is 1.8.[14b] These figures probably reflect more accurately the increase in acidity in going from toluene to the isopropylbenzene radical cation. In the present case, Φ_{lim} refers to a complex process of which proton transfer is a part, and other factors, e.g., π interaction between the benzene and naphthalene rings favoring formation of the adducts, are determining. The interaction within the radical ion couple reaches an optimum in the case of ($NDN^{\bullet-}$,,, $\mathbf{1}^{\bullet+}$), as shown by the lack of deuterium effect and the increase in Φ_{lim} (4.3 times that measured for toluene, whereas in the trifluoroacetophenone reaction the ratio is 1.4[14b]).

Notice also that for the second proton transfer in compound **8a** (the proton at the bridge position), direct transfer is even more predominant over water-mediated transfer than in the case of the benzylic proton, a trend which is common to the other cases discussed in the following. Apparently, steric overcrowding at the benzylic position induces a conformation more favorable for proton transfer from the ortho position (vide infra, Scheme Ib, **25**).

As for the stereochemistry, deuterium incorporation at the bridge position in products of structure **8** in every case involves virtually only the exo proton (distinguished from its smaller coupling constant with the bridgehead position). This reveals that also this proton transfer takes place stereoselectively, just as the proton transfer to the position α to the cyano group in compounds **8** and **9**.

The results with bibenzyl (**4**) are similar. With 0.1% D_2O deuterium incorporation is incomplete, and only with 1% D_2O does it reach 100% as far as the position α to the cyano group is concerned, while remaining only partial at the bridge position. Under this condition, however, another change is observed; the overall reaction rate is diminished and the product distribution changed in the sense that the yield of the adducts **8d**–**11d** is decreased in favor of slowly eluting products, including the monoamide **18** as well as unidentified products (polymers?) containing hydroxyl groups (compare the formation of the 3-hydroxy derivative from 1-naphthalenecarbonitrile in the presence of durene and water[15]).

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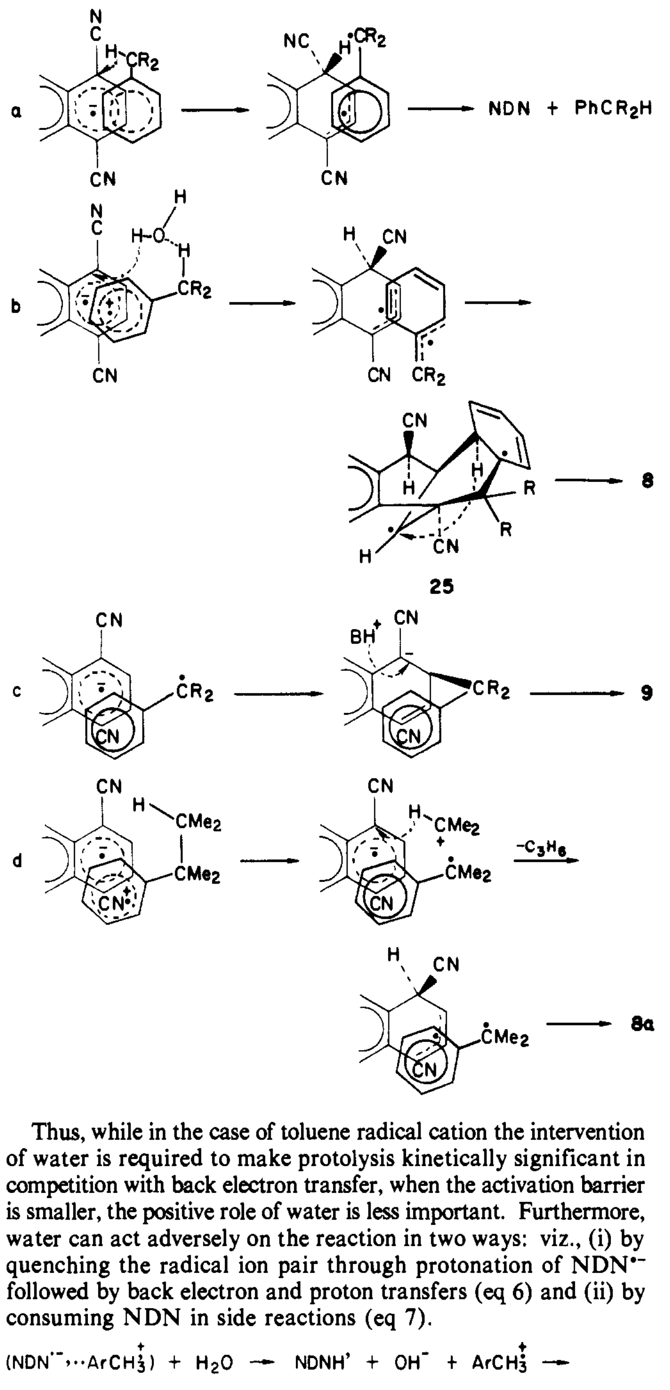
[15] Albini, A.; Spreti, S. *Tetrahedron* **1984**, *40*, 2975.

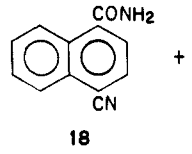
Scheme I



Thus, while in the case of toluene radical cation the intervention of water is required to make protolysis kinetically significant in competition with back electron transfer, when the activation barrier is smaller, the positive role of water is less important. Furthermore, water can act adversely on the reaction in two ways: viz., (i) by quenching the radical ion pair through protonation of NDN$^{\bullet-}$ followed by back electron and proton transfers (eq 6) and (ii) by consuming NDN in side reactions (eq 7).

$$(\mathrm{NDN}^{\bullet-}\cdots\mathrm{ArCH}_3^{\bullet+}) + \mathrm{H_2O} \rightarrow \mathrm{NDNH}^{\bullet} + \mathrm{OH}^- + \mathrm{ArCH}_3^{\bullet+} \rightarrow$$
$$\mathrm{NDNH}^+ + \mathrm{OH}^- + \mathrm{ArCH_3} \rightarrow \mathrm{NDN} + \mathrm{H_2O} + \mathrm{ArCH_3} \quad (6)$$

$$\underset{\mathbf{19}}{(\mathrm{NDN}^{\bullet-}\cdots\mathrm{ArCH}_3^{\bullet+})} + \mathrm{H_2O} \rightarrow \mathrm{ArCH_3} +$$



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$+$ hydroxylated NDN (7)

Radical ions pair **19** can be quenched by electron transfer other than proton transfer. Thus, none of these reactions take place in air-equilibrated solution,[16] as electron transfer from NDN$^{\bullet-}$ to oxygen is exothermic. Likewise a good donor such as hydroquinone dimethyl ether quenches the reaction of NDN with both **1** and **4** even at a concentration low enough to avoid quenching of NDN^{1*}, as it reduces ArCH$_3^{\bullet+}$.

Discussion

It is apparent that the reaction discussed above involves electron transfer to the NDN excited singlet followed by C–H bond cleavage or, in the case of bibenzyls, C–H and/or C–C bond cleavage and formation of new bonds to yield adducts **8**–**11**. However, the product distribution is at first sight puzzling. Thus, the tetracyclic derivative **8a** is the main product from the reaction of NDN with both **1**, where the dimethylbenzyl group which is incorporated arises from C–H bond cleavage, and **3**, where it results from cleavage of a C–C bond. However, **8a** is not formed at all in the reaction with **5**, although a derivative containing the same dimethylbenzyl group, again arising from C–C cleavage, viz., the cis adduct in position 2, is obtained in high yield. Furthermore, both bibenzyl (**4**) and its 4,4'-dimethoxy derivative **6** undergo exclusively cleavage of a C–H bond. In the first case the process observed is addition to NDN, the main product being **8c**, while in the latter case substitution of a cyano group, obtained only in traces with **4**, is the only photoprocess observed.

These differences must be related to the intervention of different species (e.g., radicals, radical ions, ions) and/or to a different order in the occurring of the various steps involved in this complex reaction (e.g., does cleavage of the radical cation precede or follow escape from the solvent cage). Therefore the appealing possibility exists that if a rationalization of the results with the various donors can be arrived at, this will at the same time solve the problem of the detailed mechanism of this reaction.

A clue is found in the comparison of the reaction of NDN with isopropylbenzene (**1**) and 2,3-dimethyl-2,3-diphenylbutane (**5**). In both cases the photoproducts result from the formal addition of a dimethylbenzyl radical and a hydrogen atom, but with **1**, product **8a** largely predominates with **9a** as a minor product, while the latter is the only product with **5**. As in the first case the donor undergoes C–H bond cleavage, and in the latter C–C bond cleavage, we conclude that the pathways in eq 8 and 9 are operative.

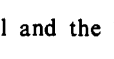
$$(\mathrm{NDN}^{\bullet-}\cdots\mathrm{ArCR_2H}^{\bullet+}) \longrightarrow (\mathrm{NDNH}^{\bullet}\cdots\mathrm{ArCR}_2^{\bullet}) \rightarrow \mathbf{8} \quad (8)$$

$$(\mathrm{NDN}^{\bullet-}\cdots\mathrm{ArCR_2H}^{\bullet+}) \xrightarrow{\mathrm{B}\ \ \mathrm{BH}^+} (\mathrm{NDN}^{\bullet-}\cdots\mathrm{ArCR}_2^{\bullet}) \xrightarrow{\mathrm{BH}^+\ \ \mathrm{B}} \mathbf{9} \quad (9a)$$

$$(\mathrm{NDN}^{\bullet-}\cdots\mathrm{ArCR_2CR_2Ar}^{\bullet+}) \xrightarrow{-\mathrm{ArCR}_2^+} (\mathrm{NDN}^{\bullet-}\cdots\mathrm{ArCR}_2^{\bullet}) \quad (9b)$$

Thus in the case of **1**, direct or base-catalyzed proton transfer leads to a radical pair which undergoes 3 + 3 addition and hydrogen shift leading to product **8** (eq 8). A second, and apparently less favored, pathway is possible for **1**, viz., proton transfer to a base and reaction of the radical with NDN$^{\bullet-}$ before the latter is protonated (eq 9a). To the same result leads eq 9b, the only pathway available for bibenzyl. In this case, the corresponding radical cation undergoes C–C bond cleavage, the carbonium ion escaping and the radical reacting in cage. In polar media the cation ArCR$_2^+$ is more stabilized than the radical ArCR$_2^{\bullet}$, so that the former diffuses and the latter reacts in cage with NDN$^{\bullet-}$ (eq 9b) in preference to the reverse process. This is supported by the trapping of the cation by nucleophiles (see below).

Examination of the stereochemistry of the products in light of this rough scheme evidences more facets of the mechanism. The radical cation and the radical anion in the singlet complex lie parallel to each other. Proton transfer can occur in either of two ways. Transfer to the nearest face of NDN$^{\bullet-}$ (Scheme Ia) is ineffective, as hydrogen exchange leading back to the starting material is favored over radical combination. Proton transfer over a long distance to the opposite face of the radical anion, as possible through water or solvent mediation (Scheme Ib), minimizes hydrogen exchange and brings the two neutral radicals in a configuration favorable for following addition, having thereby dictated the configuration of the center



The ensuing 3 + 3 cycloaddition between the benzyl radical and the "acrylic" radical in the

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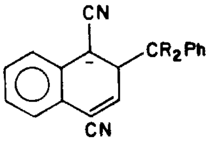
[16] However, under this condition oxygenated products are formed, compare ref 10 and 11.

naphthalene moiety has little precedent but can be rationalized as it involves extrema of maximum density in the SOMO of both radicals, and the orbital phase is matching,[17] As evidenced above in connection with the deuteration experiment, the proton enters the bridge position in **8** from the exo, and least hindered, side, thus supporting the notion that this is the last step in the process. Thus, in the deuterated product **8a′**, *four* sp^3 centers are formed in a single reaction with strict selectivity. For two of them the configuration is determined in the suprafacial cycloaddition; two are due to selectivity in proton transfer for the reason discussed. Obviously in the undeuterated product **8a**, three centers are formed stereoselectively.

On the other hand, if the benzyl radical formed according to either eq 9a or 9b reacts with unprotonated $NDN^{\bullet-}$, the anion **21** results (Scheme Ic). This species is then protonated from the least-hindered side, and this results in the cis arrangement of the substituents. The preference for the attack at position 2 probably results from the bulkiness of the dimethylbenzyl radical, which hinders formation of a new bond in position 1, where a cyano group is already present. However, with less bulky radicals, e.g., 1,2-diphenylethyl from **4**, a sizable amount of product **10**, arising from anion **22** rather than **21**, is formed.[18]



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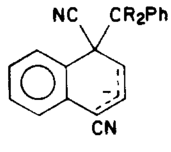

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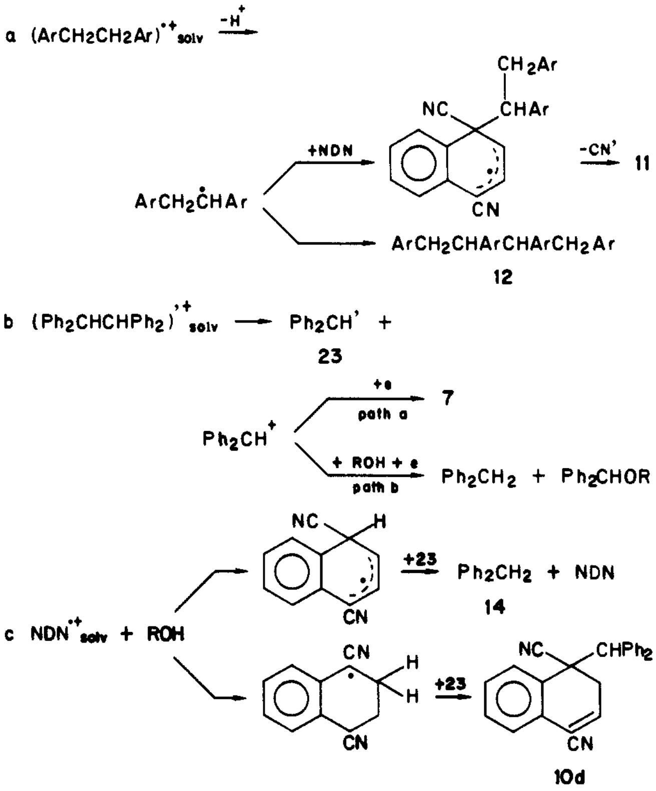
The scheme discussed above holds throughout the series of donors. Thus, bibenzyls reacting via C–C bond cleavage, such as **5** and **7**, yield **9** as the only adduct, whereas alkylbenzenes with a benzylic hydrogen or bibenzyls undergoing C–H bond cleavage, such as toluene, **1**, and **4** yield **8** with minor amounts of **9**. An apparent exception is represented by product **3**, which does undergo C–C cleavage but gives **8** and not **9** as the main product. This is easily reconciled with the above scheme when it is considered that, rather than the stable benzylic cations of the previous cases which easily escape out of cage, cleavage of **3** affords the unstable and acidic isopropyl cation which easily transfers a proton to $NDN^{\bullet-}$ in the correct position, thus functioning as a "built-in" base (Scheme Id). It has been seen above, however, that, in the presence of a relatively large amount of water, proton transfer is water mediated also in this case.

All the reactions discussed so far take place within the solvent cage and the products are formed with rigorous stereoselectivity. However, if the radical cation formed in the original electron transfer is sufficiently stable, it escapes intact out of the solvent cage and originates a different sequence of reactions. A case at hand is the dimethoxybibenzyl **6**. In this case, products **8**–**10** are not formed despite, or better because of, the high efficiency of electron transfer to NDN^{1*}, which yields in this case a stable, solvated radical cation separated from its countepart (Scheme IIa). Proton transfer to the solvent yields a "free" benzyl radical, and reaction of the latter with ground-state NDN causes substitution of a cyano group rather than the addition process observed when the benzyl radical reacts with $NDN^{\bullet-}$ before diffusing apart. We had previously shown that free benzylic radicals generated by independent methods react in this way with NDN[9] and that cyano substitution becomes more important in the photochemical reaction of NDN with very good donors, such as *p*-methoxytoluene,[19a] which conceivably give rise to separated, solvent-stabilized radical cations.

Reactions out of cage need to be considered also in the reaction of NDN with tetraphenylethane (**7**) and are clearly distinguished from the in-cage addition leading to **9d**, the yield of which is not influenced by the presence of nucleophiles. Solvent trapping products are obtained, viz., benzophenone (**13**) diphenylmethane (**14**), diphenylmethyl methyl ether (**15**). This is a photosensitization of a reaction of **7** by NDN as, at least in experiment 9 (Table I), the reaction of the former (to yield **14** and **15**) clearly exceeds consumption of the latter.

Scheme II



A different out-of-cage reaction is considered by Das. He reports that benzydryl radicals (**23**) are formed in good yield on NDN sensitization, although in a relatively slow process (τ = 160 ns, Φ 0.4).[11] However, quantum yield for the irreversible reaction we observe remains low ($\Phi_{\lim} \simeq 0.02$), and thus the benzydryl radical and the corresponding cation (**24**), even if formed efficiently, essentially undergo back electron transfer and recombination to **7**, at least in the absence of oxygen (Scheme IIb, path a). Apparently, radical **23** is too bulky to react with NDN, a reaction already slow with the less-hindered 1,2-diphenyl radical from **6** (see above).

The reaction with nucleophiles we observe is attributed to trapping of the benzydryl cation, yielding the ether **15** (as well as diphenylmethane through back electron transfer) in the case of methanol (Scheme IIb, path b) (In the meantime, Arnold has reported the cleavage of tetraphenylethane after electron transfer to 1,4-dicyanobenzene and the ensuing reaction with methanol. Okamoto, A.; Arnold, D. R. *Can. J. Chem.* **1985**, *63*, 2340). In the presence of water, benzophenone, rather than the expected benzhydrol is obtained. In a separate experiment we observed that the latter is rapidly dehydrogenated in the presence of NDN. Thus, the formation of benzophenone can be due to a secondary process.

In the presence of a larger amount of methanol (experiment 9) the ether **15** is still formed, but the amount of diphenylmethane increases beyond consumption of NDN.

The reaction can be considered a reductive cleavage of tetraphenylethane at the expense of methanol under sensitization by NDN. As hydrogen abstraction from methanol by benzydryl radicals is endothermic, this process is not related to the formation of radicals revealed by flash photolysis. A plausible mechanism for indirect reduction is that at this high concentration methanol intercepts the radical ion couple and protonates NDN, largely at position 1 and less at position 2. The persistence of benzydryl radical makes its reaction with these two naphthyl radicals likely,

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[17] Compare ref 9, Figure 3.

[18] In the reaction with durene, products **9** and **10** are formed in 25% yield each, ref 8.

[19] (a) Albini, A.; Fasani, E.; Montessoro, E. *Z. Naturforsch., B* **1984**, *29b*, 1409. (b) Albini, A.; Arnold, D. R. *Can. J. Chem.* **1978**, *56*, 2985.

leading in the first case to diphenylmethane (**14**), in the latter to the adduct **10d** (Scheme IIc). This explains the small decreases in the yield of the in-cage adduct **9** and the formation of the adduct at C-1 (**10d**) under this condition.

That nucleophile trapping is observed with diphenylmethyl cation and not with dimethylbenzyl cation formed by cleavage of **5** is explained by the rapid deprotonation of the latter to α-methylstyrene, in turn undergoing polymerization under the reaction condition.

Conclusion

The interaction between 1,4-naphthalenedicarbonitrile and alkylbenzenes or bibenzyls is revealed by exciplex emission in apolar solvents. Polar solvents favor charge transfer and stabilize the radical ions pair. Chemical reaction depends on in-cage benzylic proton transfer from the radical cation to $NDN^{\bullet -}$, in competition with back electron transfer or diffusion out of cage. The present results, in accordance with previous work,[9] show that proton transfer can be rapid, its rate reaching 42% of the competing processes ($\Phi_{\lim} = k_r/(k_r + k_d) = 30\%$, Table III) in the case of isopropylbenzene (**1**), to be compared with 8% in the cas of toluene.[9] Carbon–carbon bond cleavage also occurs in radical cations when carbon–hydrogen bond cleavage is impossible, as in the case of donors **3** and **5**, or less favored from the thermodynamic point of view, as in the case of donor **7**. However, as it involves heavier atoms, this latter process is intrinsically slower, with a rate not higher than 2% of the back-electron-transfer rate. Under our condition, out-of-cage reactions, that, is electron-transfer photosensitized cleavage of the donor, is also inefficient, both when it involves C–H bond (e.g., compound **6**) or C–C bond (e.g., compound **7**) cleavage. However, it is possible that conditions of more efficient trapping will minimize recombination and reveal that these processes are relatively efficient.

We cannot compare our results quantitatively with the recent report by Reichel et al. about NDN-sensitized cleavage of bibenzyls. They report the yield of transients,[11] whereas we report the quantum yield of steady-state photoreactions. More importantly, two different phenomena are looked at: the formation of solvent-separated, solvated radical ions and radicals in their case, in contrast to the in-cage reaction, which must occur in a very short time scale in our case.

Both types of reactions are synthetically interesting. Photosensitized formation of solvated radical ions offers new possibilities of benzylic funtionalization, certainly to be exploited beyond the presently known oxygenation.[10] On the other side, in-cage recombination is specially attractive because of the strict stereoselectivity in the formation of adducts **8** and **9**, potentially useful synthons.

Experimental Section

1,4-Naphthalenedicarbonitrile was prepared and purified as previously described.[19b] Spectrograde acetonitrile was used as obtained or was dried by refluxing and distilling over CaH_2. Isopropylbenzene (**1**), *tert*-butylbenene (**2**), and bibenzyl (**4**) were commercial products and were purified by fractional distillation or recrystallization.

(1,1,2-Trimethylpropyl)benzene (**3**), 2,2-Dimethyl-2-phenylacetic acid[20] (20 g, 122 mM) was converted to the chloride by heating on a steam bath for 1 h with thionyl chloride (16 g). To the cooled mixture was added methanol (7 mL), and the mixture was heated again on a steam bath for 1 h. Excess methanol was evaporated, and fractional distillation of the residue afforded 21.3 g (98% yield) of the methyl ester (bp 83–85 °C at 0.5 mm). Twenty-two grams (123 mM) of this ester in 20 mL of absolute ether was added in $^1/_2$ h under cooling to a solution of the Grignard prepared from 7.5 g of magnesium and 19 mL of methyl iodide in 80 mL of ether. The mixture was refluxed for 3 h while being stirred and then was decomposed in sulfuric acid–ice. Usual workup afforded 2,3-dimethyl-3-phenyl-2-butanol (bp 68–70 °C at 0.1 mm, 17.8 g, 81% yield). Dehydration of this material (15 g) in the presence of some crystals of iodine at 100 °C for 15 min yielded a mixture of alkenes (bp 65–67 °C at 1.5 mm, 12.8 g, 95% yield) which was mixed with 30 mL of ethanol and hydrogenated at normal pressure for 20 h in the presence of Pd over carbon to yield 11.7 g (90% yield) of the title compound, bp 48–50 °C at 0.1 mm [lit.[21] bp 213–214 °C].

2,3-Dimethyl-2,3-diphenylbutane (**5**) was prepared in 30% yield from isopropylphenyl chloride by the Wurz procedure[22a] and recrystallized from ethanol, mp 114–15 °C [lit.[22b] mp 115 °C].

4,4′-Dimethoxybibenzyl (**6**) was prepared according to the method by Trahanovsky,[23] purified by chromatography on alumina, and recrystallized from cyclohexane.

1,1,2,2-Tetraphenylethane (**7**) was prepared by the procedure of Gilman[24] and recrystallized from acetic acid.

Isopropylbenzene-*α*-*d* (**1′**) was prepared by the procedure of Rummel[25] via reduction of acetone with lithium aluminum deuteride, conversion of the alcohol into the bromide, and Friedel–Craft alkylation. In our hands this gave a 34% overall yield (calculated on the $LiAlD_4$) of a product boiling at 148–150 °C, with ≥98% deuteration (NMR, mass spectrum).

Preparative Photochemical Reactions. An acetonitrile solution (70 mL) containing 250 mg (1.4 mM) of NDN and 2.4 g (20 mM) of isopropylbenzene 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 (4 h, TLC). After evaporation of the solvent, the photolysate was chromatographed on silica gel, eluted with cyclohexane in order to eliminate excess **1** and then with cyclohexane–EtOAc mixtures, and yielded adducts **8a**, 185 mg (45%), and **9a**, 41 mg (10%).

Irradiation in the presence of the benzene derivatives **1**–**7** and **1′** was conducted similarly. The initial donor amount was 4–20 mM, according to their solubility in acetonitrile, and the irradiation was pursued until 50–100% of NDN was converted.

Irradiation of NDN in the presence of **2** in acetonitrile or in the presence of any of the donors **1**–**7** in cyclohexane or benzene for 8 h left NDN unchanged.

Benzophenone, diphenylmethane, and benzydryl methyl ether[26] were identical with authentic samples. All new products gave correct analytic data. The structures were assigned on the basis of their analytical and spectroscopic properties. The most significant data are reported in Table II. A discussion of the structure assignment of products of similar structure and of their spectroscopic properties is given in ref 8.

Quantitative Measurements. Fluorescence spectra were measured by means of a 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 (intensity ca. 10^{-7} einstein min^{-1} cm^{-2}) obtained from a focalized high-pressure mercury arc by means of an interference filter ($\Delta\lambda_{1/2} = 5$ nm).

Acknowledgment. This work was executed within the special project on fine chemistry supported by CNR, Rome.

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