Tetrahedron Vol. 42, No. 22, pp. 6219 to 6224, 1986
Printed in Great Britain.

0040–4020/86 $3.00+.00
Pergamon Journals Ltd.

THE PHOTOCHEMICAL REACTION OF 1,4-NAPHTHALENEDICARBONITRILE WITH AROMATIC PINACOLS AND PINACOL ETHERS

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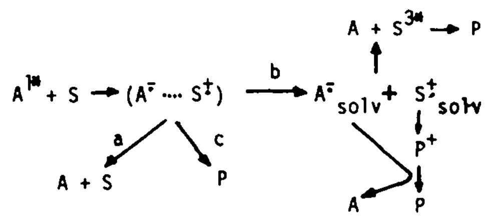
(*Received in U.S.A.* 15 *December* 1985)

Abstract—Irradiation of 1,4-naphthalenedicarbonitrile (NDN) in deoxygenated acetonitrile in the presence of aromatic pinacols (**1**) leads to reduction of the former to the dihydro derivative **4** and the tetrahydro derivative **5** as well as to oxidative cleavage of the latter to yield ketones or aldehydes (**3**). Reaction with pinacol ethers (**2**) leads to product types **3**, **4** and **5** as well as to 1(1-methoxybenzyl)-1,2-dihydro NDN derivatives (two diastereoisomers, **6** and **7**). Only one of these adducts is formed in the reaction of NDN with benzyl methyl ether (**8**). The reaction involves electron transfer to singlet excited NDN and cleavage of the radical cations $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ to yield α-hydroxy and α-methoxy radicals, respectively. These react with NDN by proton transfer in the first case, and by carbon–carbon bond formation in the latter. The stereoselectivity observed in the adduct formation with **8** is explained by deprotonation of the radical cation and reaction of the corresponding radical with $NDN^{\cdot-}$ in the geminate solvent cage. The mechanism of these reactions is discussed in the light of a recent flash-photolysis study.

The interaction of a singlet excited aromatic molecule (A^{1*}) with a variety of substrates (S) leads, when this is thermodynamically feasible, to electron transfer and the generation of a pair of radical ions, in most reported cases the radical anion $A^{\cdot-}$ and the radical cation $S^{\cdot+}$. Energy wasting back electron transfer (Scheme 1, path a), then competes with separation of the radical ions and reaction of solvated $S^{\cdot+}$. The aromatic molecule can act either as an electron transfer photosensitizer in a reaction of S (path b), or by in-cage reaction between the radical ions (path c). Although back electron transfer between the spin paired radical ions is obviously a very fast process, a large variety of electron transfer initiated photochemical reactions occur with a quantum yield high enough to make them useful from the synthetic point of view.

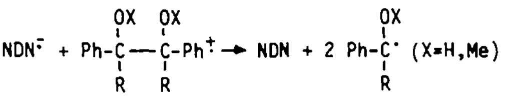
Most reported photosensitized reactions involve isomerization, fragmentation or addition to alkenes,[1] alkynes[2] or three- or four-membered cyclic derivatives.[3] These reactions have been shown to occur by either of two mechanisms, namely chemical reaction of the solvated radical cation $S^{\cdot+}$ to yield a product P, back electron transfer from $A^{\cdot-}$ intervening at some intermediate stage, or back electron transfer to yield the substrate triplet, if the energy of the latter is lower than that of the radical ion pair (Scheme 1). Spectroscopic studies (flash photolysis,[4] chemically induced dynamic nuclear polarization,[5] electron paramagnetic resonance[6]) have lent support to the formulation of the mechanism of these sensitized reactions.



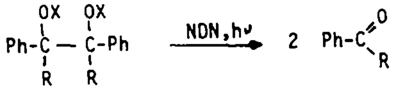
Scheme 1.

In-cage direct reaction between the radical ions is less well characterized from the spectroscopic point of view. Apart from cycloadditions, in which the role of intermediate radical ions might be more important than hitherto suspected,[7] such reactions involve proton transfer or cleavage of weak bonds. Thus, we have shown that the photochemical reaction between 1,4-naphthalenedicarbonitrile (NDN) and methylbenzenes[8] involves electron transfer followed by proton transfer and stereoselective reaction of the radical pair. Likewise, bibenzyls undergo carbon–carbon bond cleavage after electron transfer to excited NDN, and the resulting benzyl radical reacts in cage with the NDN radical anion.[9] With both classes of compounds, however, strongly stabilized radical cations diffuse out of cage and undergo different reactions.[8c,9]

In view of this experience, we were particularly interested in a paper by Das and co-workers stating that pinacols and pinacol ethers fragment under sensitization by NDN.[10] As the amount of ketyl radicals observed far exceeds the amount of $NDN^{\cdot-}$, it was assumed that back electron transfer between the radical ion pair leads to fragmentation (Eq. 1). From the preparative point of view, the same authors report that NDN causes oxidative cleavage of these substrates to ketones (Eq. 2).[11]



$$NDN^{\cdot-} + Ph\text{-}\underset{R}{\overset{OX}{C}}\text{—}\underset{R}{\overset{OX}{C}}\text{-}Ph^{\cdot+} \longrightarrow NDN + 2\ Ph\text{-}\underset{R}{\overset{OX}{C}}{}^{\cdot}\ (X{=}H,Me) \quad (1)$$



$$Ph\text{-}\underset{R}{\overset{OX}{C}}\text{—}\underset{R}{\overset{OX}{C}}\text{-}Ph \xrightarrow{NDN,h\nu} 2\ Ph\text{-}C\overset{O}{\underset{R}{\lessgtr}} \quad (2)$$

It would seem that in going from bibenzyls to pinacols a change from an electron transfer initiated reaction (path c) to a photosensitized reaction (path b) takes place, and this could be due to a greater stabilization of the radical cation which escapes more

Table 1. Preparative irradiation of NDN in the presence of substrates **1**, **2**, and **8**

No.	Substrate, mM	NDN, mM	Solvent	Irradiation time, h	Reacted NDN, mM (% yield)	Products, mM (% yield)[a]
1	**1a**, 41	5.5	MeCN	4	4.9(90)	**4**, 2.4(50); **5**, 0.9(18); **3a**, 14(143)
2	**1a**, 27	14	MeCN	3	10.1(72)	**4**, 8.9(88); **3a**, 10(99)
3	**1a**, 27	11	Benzene	15	0.5(5)	**4**, 0.5 (100); **3a**, 1(100)
4	**1b**, 41	5.5	MeCN	4	4.7(86)	**4**, 3(64); **5**, 0.8(17); **3b**, 15(159)
5	**1b**, 41	11	MeCN	4	6.6(60)	**4**, 5.5(83); **3b**, 16.5 (125)
6	**1c**, 41	5.5	MeCN	6	3.5(64)	**4**, 2(57); **3c**, 3.8(54)
7	**2b**, 10	14	MeCN	26	8.4(60)	**4**, 1.6(20); **3b**, 3.5(42); **6b**, 2.5(30); **7b**, 2.5(30)
8	**2b**, 10	14	MeCN, 0.2% H_2O	26	4.5(32)	**4**, 1.7(38); **5**, 1.5(33); **3b**, 5.5(122); **6b**, **7b**, traces
9	**2b**, 10	14	MeCN, 2% MeOH	26	8(57)	**4**, 2.6(33); **3b**, 6(75); **6b**, 0.8(10); **7b**, 0.8(10)
10	**2c**, 30	14	MeCN	26	2.8(20)	**4**, 1.6(57); **3c**, 3.3(59); **6c**, 1.2(42); **7c**, 1.2(42)
11	**8**, 130	11	MeCN	27	7.2(65)	**4**, 0.6(8); **2c**, 0.6(17); **6c**, 5.2(72)

[a] Isolated yields after column chromatography are reported, or in the case of ketones, VPC determined yields. Yields are calculated taking into account that 2 mol of ketone are formed from the pinacols and pinacol ethers.

readily and finds new chemical pathways available. The reaction according to Eq. (2), however, is not straightforward, as the reduction product complementary to the oxidized pinacols was not identified.

For these reasons it appeared worthwhile to reinvestigate the photochemical reaction between NDN and aromatic pinacols (**1**) and pinacol ethers (**2**) in the absence of oxygen and to determine all occurring chemical processes and their quantum yields.

RESULTS AND DISCUSSION

The most relevant preparative data are summarized in Scheme 2 and Table 1, and quantum yield measurements are reported in Table 2.

Table 2. Reaction quantum yield

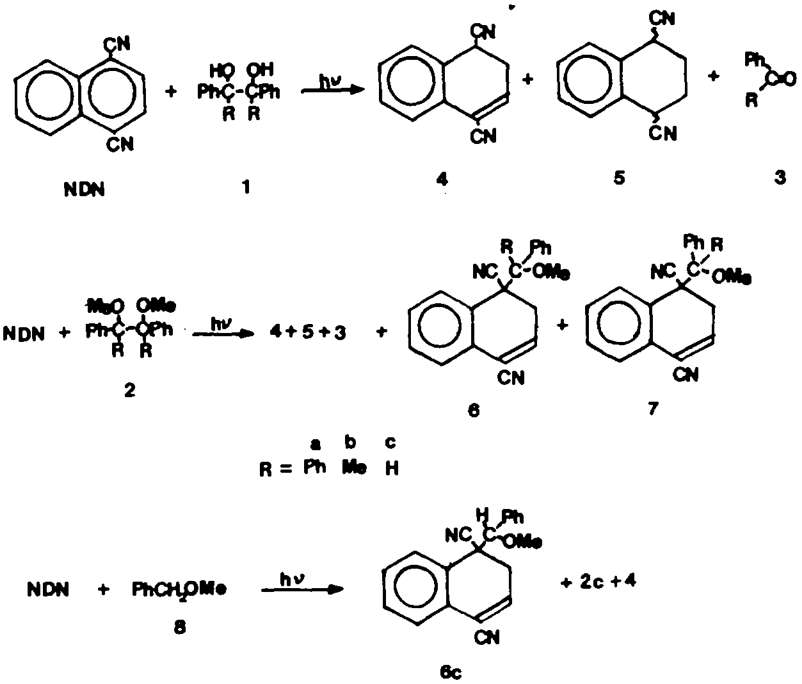
Substrate[a]	α[b]	Φ_{reac}	Φ_{rad}[c]
1a	0.7	0.14	0.5
1b	0.67	0.025	0.095
1c	0.66	0.008	
2b[d]	0.25	0.02	
2c	0.32	0.005	

[a] Substrate concentration 0.02 M.

[b] Fraction of the NDN singlet quenched by the substrate.

[c] Quantum yield for radical formation according to Ref. 10.

[d] Substrate 0.005 M.



Scheme 2.

Reaction of NDN with pinacols

In our hands, irradiation (Pyrex filtered) of a 5.5 mM solution of NDN in deoxygenated acetonitrile in the presence of a large excess (41 mM) of benzopinacol (**1a**) led to consumption of both reagents. When 90% of the dinitrile has reacted, 7.2 mM benzopinacol are consumed and correspondingly 14 mM benzophenone (**3a**) are formed. NDN is reduced, mainly to 1,2-dihydro-1,4-naphthalenedicarbonitrile (**4**) and further to a mixture of *cis*- and *trans* - 1,2,3,4 - tetrahydro - 1,4 - naphthalenedicarbonitrile (**5**). In several other experiments, the irradiation was interrupted at an earlier stage, or different molar concentrations of either NDN or **1a** were used. In no case did the ratio of NDN reduced to **1a** oxidatively cleaved exceed 1.5. The main NDN derived product was **4**, with increasing amounts of **5** at higher conversion.

Therefore, NDN is not a sensitizer in the true sense, but a reagent, and the observed reaction obeys the stoichiometry shown in Eqs (3) and (4), the latter reaction occurring only partially under these conditions.

$$\mathrm{NDN} + \mathrm{Ph_2C(OH)CPh_2OH} \xrightarrow{h\nu} \mathrm{NDNH_2}\ (\underset{\sim}{4}) + 2\ \mathrm{Ph_2CO} \quad (3)$$

$$\mathrm{NDNH_2} + \mathrm{Ph_2C(OH)CPh_2OH} \xrightarrow{h\nu} \mathrm{NDNH_4}\ (\underset{\sim}{5}) + 2\ \mathrm{Ph_2CO} \quad (4)$$

Obviously, it is possible that in the presence of dissolved oxygen NDN is not consumed.† In degassed benzene, under otherwise identical conditions, only a very slow reaction takes place (entry 3, Table 1).

Reaction with other aromatic pinacols is analogous. Thus, the *meso* pinacols **1b** and **c** are oxidized to acetophenone (**3b**) and benzaldehyde (**3c**), respectively, with corresponding reduction of NDN as shown above (entries 4–6, Table 1).

Reaction of NDN with pinacol ethers

In the photochemical reaction with pinacol ethers NDN is again a reagent and not a sensitizer. The reaction course is more complex in that adduct formation takes place together with oxidative cleavage of the ethers and reduction of NDN.

Thus, irradiation of NDN in the presence of *meso* 2,3-dimethoxy-2,3-diphenylbutane (**2b**) yields 1.6 mM dihydro NDN, 3.5 mM acetophenone and 2.5 mM each of the two adducts **6b** and **7b**, when 8.4 mM of the nitrile are consumed. The adducts can be recognized from their composition and their spectroscopic properties as the two diastereoisomeric 1,2-dihydronaphthalenes carrying a (1-methoxy-1-phenyl) ethyl group in position 1 (Scheme 2). The relevant NMR and IR spectroscopic properties are listed in Table 3.

As the adduct formation might involve the intervention of moisture present in solution, the same reaction was conducted in the presence of small amounts of water or methanol (entries 8 and 9, Table 1). However, this leads to a substantial decrease in the formation of adducts **6b** and **7b** and an increase in the yield of acetophenone.

The reaction of the pinacol ether **2c** is slower but proceeds analogously to yield adducts **6c** and **7c** as well as benzaldehyde and reduced NDN.

Reaction of NDN with benzyl methyl ether

Adducts **6** and **7** can be explained by addition of a methoxybenzyl radical, an intermediate which, in principle, can be obtained by an alternative pathway, namely deprotonation of a benzylic radical cation. To test this hypothesis, we irradiated NDN in the presence of benzyl methyl ether **8** (entry 11, Table 1) in deoxygenated acetonitrile. Indeed addition takes place, but only one of the diastereoisomers is formed (**6c**). Minor products are the pinacol ether **2c** and reduced NDN (**4**).

Control experiments showed that under our conditions NDN does not undergo measurable reduction when irradiated either in dry acetonitrile or in the presence of water or methanol, nor do the donors **1**, **2** and **8** undergo any decomposition when irradiated in the absence of NDN.

Quantum yield measurements

The total quantum yield for reaction of NDN in the presence of 20 mM pinacol and pinacol ether, measured in degassed acetonitrile ranges from 0.005 to 0.14 (Table 2). Taking into account that the NDN singlet is only partially quenched by the donor (fraction α in Table 2), this shows that the efficiency for irreversible chemical reaction following initial electron transfer to excited NDN ranges from 0.015 to 0.2. The concentrations used in these measurements were similar to those of the flash photolysis experiments by Das and co-workers,[11] although, of course, the light flux was not. Nevertheless, a meaningful

Table 3. Relevant properties of the 1-substituted 1,2-dihydro-1,4-naphthalenedicarbonitriles

Substrate	M.p., °C	NMR, δ^a Olefinic	CH_2	Benzylic	IR, $cm^{-1\,b}$
6b	180 (benzene)	6.1	3.3^c		2220–2240
7b	134–135 (cyclohexane)	6.4	3.25^c		2220–2240
6c	138–140 (cyclohexane)	6.85	3.35^c	4.2	2220–2240
7c	112–114 (cyclohexane)	6.9	3.2^c	4.3	2220–2240
4	85–87 (benzene)	6.9	2.9^d		2220–2240

^{a}In $CDCl_3$.
^{b}In KBr.
^{c}Centre of the AB part of the ABX system.
^{d}Centre of the AB part of the ABXY system; 1-H at 4.1 δ.

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† No reaction of NDN is mentioned in Ref. 11, although up to 3 mol pinacol are oxidized even in the absence of oxygen.

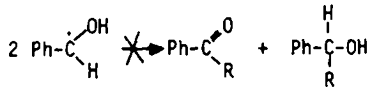
comparison should be possible. Limited variations in the concentration of NDN do not change the value of Φ, and variations in the concentration of the donors change Φ proportionally to α.

DISCUSSION

There is little doubt that the decomposition of pinacols and pinacol ethers **1** and **2** involves the respective radical cations formed by electron transfer to singlet excited NDN. In benzene, quenching of NDN^{1*} is much less efficient and so is the chemical reaction (entry 3, Table 1). Furthermore, cleavage of the central carbon–carbon bond in products **1** and **2** is expected to be a facile process. Benzopinacol and its ethers are used as polymerization initiators[12] because of the low activation energy for homolytic cleavage.[13] The activation energy for the cleavage of benzopinacol in benzene is $\Delta E_A = 33$ kcal M^{-1}, corresponding to a bond dissociation energy of 32 kcal M^{-1} in benzene; in polar solvents both values are lower as the radicals are stabilized through hydrogen bonding to the solvent.[14] As for the cleavage of pinacol ethers, the ΔE_A for compound **2b** is ~47 kcal M^{-1}.[15] Thus, NDN sensitized cleavage of pinacols and pinacol ethers is energetically feasible.

Furthermore, there is abundant evidence that chemical oxidation initiates cleavage of benzopinacol and related compounds. Both organic[16] and inorganic oxidizers[17] and active in this sense and in some cases the reaction is catalytic.[18]

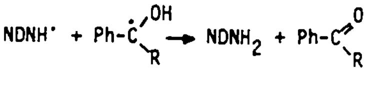
Thus, it appears possible that, as represented in Ref. 10, NDN sensitizes homolytic cleavage of pinacols via back-electron transfer within the initially generated radical ion pair (Eq. 1), although completion of the reaction requires that NDN intervenes again, this time as a reagent, through quenching of the ketyl radicals. It is consistent with this scheme that both the radical yield measured by flash photolysis and the product yield measured under steady state conditions decrease with decreasing radical stabilization (R = Ph, Me, H). However, the former quantity is much larger than the latter. It follows that recombination is the major pathway by which the ketyl radicals are depleted. No significant disproportionation takes place, as no benzhydrol (Eq. 5) is formed. This conclusion is in accord with the observation by Weiner[14] that for structure and solvent stabilized ketyl radicals recombination is the preferred pathway.



$$2\ \mathrm{Ph{-}\dot{C}(OH)H} \not\longrightarrow \mathrm{Ph{-}C(=O)R} + \mathrm{Ph{-}CH(OH)R} \qquad (5)$$

In the case of benzopinacol, about 50% of the radical cations are cleaved into ketyl radicals, according to flash photolysis evidence. We find that only 20% undergo irreversible reaction. Thus, about 40% of the radicals transfer a hydrogen atom to NDN or NDNH$^{\cdot}$ (Eqs 6 and 7) whereas 60% recombine.

$$\mathrm{NDN} + \mathrm{Ph{-}\dot{C}(OH)R} \longrightarrow \mathrm{NDNH^{\cdot}} + \mathrm{Ph{-}C(=O)R} \qquad (6)$$



$$\mathrm{NDNH^{\cdot}} + \mathrm{Ph{-}\dot{C}(OH)R} \longrightarrow \mathrm{NDNH_2} + \mathrm{Ph{-}C(=O)R} \qquad (7)$$

Previously it has been shown that ketyl radicals are trapped by maleic acid derivatives with formation of carbon–carbon bonds[13a] while in the present case proton transfer apparently predominates.

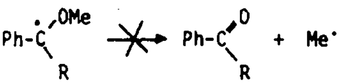
An alternative rationalization involves proton transfer within the original radical ion pair followed by cleavage of the alkoxy radical **9** (Scheme 3). Such an intermediate has been postulated previously to explain the oxidative cleavage of benzopinacol promoted by various agents.[13b,14c,16] This pathway might be a source of ketyl radicals alternative to Eq. (1), or even the exclusive source, as the yield of ketyl radicals revealed by flash photolysis does not exceed 50% of the theoretical. However, in the latter hypothesis, the quantum yield of irreversible reaction should also be 50%. Considering that the radical yield is higher with pinacol ethers than with pinacols,[10] it can be speculated that two concurrent pathways exist, namely:

(a) carbon–carbon bond cleavage according to Eq. (1), with ensuing radical recombination and thus, no net reaction, and

(b) proton transfer from the hydroxyl group, obviously possible only for the pinacols, leading irreversibly to ketones according to Scheme 3.

As for the reaction of NDN with pinacol ethers, the quantum yield we observe for the steady state reaction is again low. Thus, although α-methoxybenzyl radicals are efficiently formed, as revealed by flash photolysis, they essentially recombine (Eq. 8). Cleavage to yield a methyl radical and a ketone (Eq. 9) is energetically unfavourable and remains a minor pathway at room temperature, in accord with literature reports.[20]

$$2\ \mathrm{Ph{-}\dot{C}(OMe)R} \longrightarrow \mathrm{Ph{-}C(OMe)(R){-}C(OMe)(R){-}Ph} \qquad (8)$$

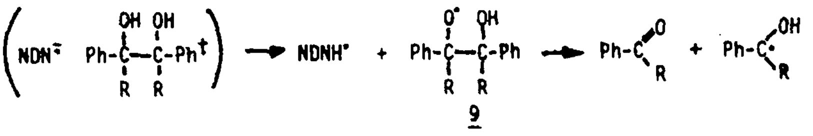


$$\mathrm{Ph{-}\dot{C}(OMe)R} \not\longrightarrow \mathrm{Ph{-}C(=O)R} + \mathrm{Me^{\cdot}} \qquad (9)$$

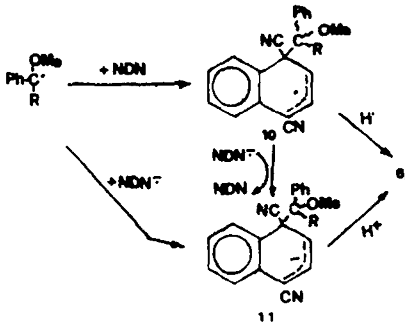
Starting with the *meso* pinacol ethers **2** we found no isomerization to the DL form, in accord with Das and co-workers.[11] Conversely, they report that the DL form is partially isomerized to the *meso* form under these conditions. This is again in accordance with a recombination mechanism being operative.

Reaction of the methoxybenzyl radicals with NDN or its radical anion leads to carbon–carbon bond formation and results in products **6** and **7**. In the first case radical **10** would arise, in the latter the corresponding anion **11**, possibly arising also from NDN$^{\cdot -}$ reduction of radical **10** (Scheme 4). The final step of this mechanism requires hydrogen abstraction by radical **10** or protonation of anion **11** by traces of moisture.

However, addition of known amounts of water (or methanol) decreases the yield of the adducts and enhances the yield of the ketone. The former effect is explained by protonation of NDN$^{\cdot -}$ in the radical ion pair competing with the following coupling reaction, just as it happens in the photochemical reaction of NDN with bibenzyls.[9] The latter effect suggests that, when a nucleophile is present, the ketone is formed at least in part from the methoxybenzyl cation rather

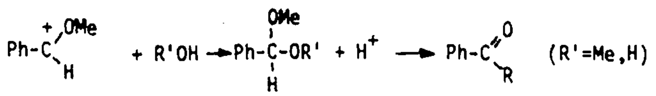


Scheme 3.



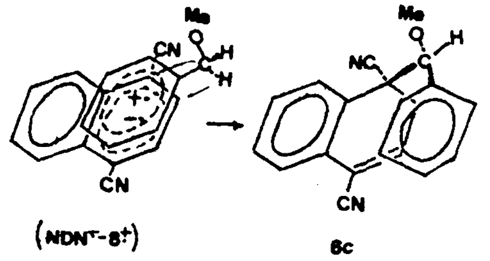
Scheme 4.

than from the corresponding radical (Eq. 10).†



$$Ph{-}\overset{+}{C}(OMe)H + R'OH \longrightarrow Ph{-}C(OMe)(H){-}OR' + H^{+} \longrightarrow Ph{-}C(=O)R \quad (R'=Me,H) \qquad (10)$$

Finally, the reaction with benzyl methyl ether is in part analogous to the reaction with **2c**, in that deprotonation of the radical cation $\mathbf{8}^{+}$ leads to the same benzyl radical, which in part recombines to **2c**, and in part yields benzaldehyde. However, the formation of a single adduct instead of the two diastereoisomeric adducts formed from **2c** points to a different mechanism for the addition process. This can be rationalized if a fast reaction takes place within the radical ion pair before diffusion out of cage. In this case transfer of a benzylic proton and formation of the new carbon–carbon bond take place on the same side of the naphthalene ring. Thus, if, as is reasonable, the excited complex between benzyl methyl ether and NDN has a preferred conformation, e.g. with the phenyl ring lying parallel over the naphthalene ring and the methoxy group pointing outside in order to minimize steric interaction, reaction results selectively in a couple of enantiomers, reflecting the preferred stereochemistry in the initial charge transfer complex (Scheme 5). We are not able at the moment to assign the stereochemistry of product **6**,‡ but the fact remains that such a pathway explains the stereoselectivity observed with **8**, whereas cleavage of pinacol ether **2c** yields "free" α-methoxybenzyl radicals and these react with NDN yielding both diastereoisomers **6c** and **7c** (thereby proving that **6c** is not preferentially formed because of steric restrictions).



Scheme 5.

CONCLUSION

In conclusion, we have shown that in pinacols and pinacol ethers the strongly stabilizing effect of hydroxy and methoxy groups facilitates diffusion and solvation of the radical cations formed by electron transfer to excited NDN and following cleavage to yield α-hydroxy- or α-methoxybenzyl radicals. These recombine or react with NDN, which acts not only as an electron transfer sensitizer but also as a reagent. In the case of pinacols, the reaction leads to reduced NDN and ketone, in the case of pinacol ethers it leads to adducts.

Addition is observed also with benzyl methyl ether, but this is a different process, involving fast proton transfer and coupling of the radicals before they diffuse apart, thus yielding stereoselectively one of the two possible diastereoisomeric adducts.

More generally, we think that this study shows that rationalization of inherently multistep processes such as photochemical electron transfer reactions requires analysis from different points of view, so that pieces of evidence from different sources complement each other and contribute to formulate a detailed mechanism.

EXPERIMENTAL

1,4-Naphthalenedicarbonitrile was prepared and purified as previously described.[21] Spectrograde acetonitrile was dehydrated by refluxing and distilling over CaH_2. Benzopinacol was prepared by photochemical reduction of benzophenone,[22] pinacol **1b** by Grignard reaction of benzil,[23] and pinacol **1c** by aluminium amalgam reduction of benzil.[24] Pinacol ethers **2b** and **c** were prepared from the corresponding pinacols according to Ref. 11. Benzyl methyl ether was prepared from benzyl chloride.[25]

Photochemical reactions. An acetonitrile soln (100 ml) containing NDN and a donor in the molar concentration required (Table 1) were refluxed for a few minutes, cooled while flushing with purified Ar and irradiated with a medium

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† This shows that "free" $\mathbf{2}^{+\cdot}$ undergoes cleavage yielding a methoxybenzyl cation and a radical, although part of the reaction may occur simultaneously with back electron transfer from $NDN^{-\cdot}$, yielding directly two radicals (Eq. 1).

‡ If the preferred configuration of the complex is indeed the one depicted in Scheme 5, then product **6** corresponds to the (*R*,*R*), (*S*,*S*) enanthiomeric couple.

pressure Pyrex filtered 150 W Helios Italquartz mercury arc at 17°. After evaporation of the solvent, the raw photolysate was chromatographed on silica gel eluting with cyclohexane and cyclohexane–EtOAc mixtures. Volatile ketones were determined by VPC. Isolated products were purified by recrystallization and characterized by spectroscopic methods and elemental analysis (to $\pm 0.3\%$ of the theoretical) (Table 3). Isomeric tetrahydronaphthalenedicarbonitriles were not separated and determined by NMR in the mixture of the two.[26]

We have no element at present to assign the configuration of the diastereoisomeric pair of products **6b**/**7b** and **6c**/**7c**. Compound **6** is in both cases the first to elute.

Measurements. Fluorescence intensities were measured on an Aminco Bowman spectrophotofluorimeter in 1 cm optical path spectrophotometric couvettes using samples degassed by five freeze–degas–thaw cycles to 10^{-4} Torr. Linear Stern Volmer plots for the quenching of NDN fluorescence by donors **1a–c**, **2b,c**, **8** were obtained in every case. Chemical quantum yield was measured in similarly degassed samples, irradiated at 313 nm (interference filter) on an optical bench fitted with a high pressure 200 W Osram mercury arc (light flux *ca* 1×10^{-6} Einstein $\text{min}^{-1}\,\text{cm}^{-2}$ as determined by ferrioxalate actinometry). NDN reaction was determined spectrophotometrically and substrate consumption and ketone formation were determined by VPC. In these experiments, NDN conversion was limited to *ca* 10%.

Acknowledgement—This work was executed within the special project on fine chemistry sponsored by CNR, Rome.

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