Photochemically Induced Oxygenation of Methylbenzenes, Bibenzyls, and Pinacols in the Presence of Naphthalene-1,4-dicarbonitrile

Angelo Albini and Silvia Spreti
Dip. Chimica Organica dell'Università, V. Taramelli 10, 27100 Pavia, Italy

The photochemical reaction of aromatic donors in oxygen-saturated solution in the presence of naphthalene-1,4-dicarbonitrile (NDN) has been investigated. Methylbenzenes (**1a, b**) are found to give benzaldehydes, bibenzyls (**4a—d**) are cleaved to benzaldehydes (or phenyl ketones) and benzyl alcohols, pinacols (**7a—c**) and pinacol ethers (**9b, c**) are likewise cleaved to carbonyl derivatives (in the latter case also to esters). The mechanism of this reaction is discussed on the basis of product distribution and quantum yield both in the absence and in the presence of oxygen, and involves electron-transfer from the donors to the NDN singlet excited state and deprotonation [for compounds (**1**) or (**4a, b**)] or carbon–carbon bond cleavage [for compounds (**4c, d**), (**7**), and (**9**)] of the radical cation, followed by reaction of the benzyl radicals with oxygen.

There are many reports concerning the oxygenation of substrates photosensitized by aromatic nitriles.[1] These reactions involve electron-transfer from the substrate to the singlet excited state of the nitrile and addition of superoxide anion to the substrate cation, although in some cases the nitriles function as oxygen sensitizers and the reactive species is singlet oxygen.[2] The oxidation mechanism may involve alkenes,[3] alkynes,[4] cyclopropanes and butenes,[5] heterocyclic derivatives,[6] and sulphides.[7]

The photochemical reaction between naphthalene-1,4-dicarbonitrile (NDN) and alkylbenzenes and bibenzyls[8,9] in the presence of oxygen is found to give oxidation of the donors. This has a precedent in the photo-oxidation of some methylbenzenes sensitized by anthracene-9,10-dicarbonitrile.[10] Recently, Griffin, Das, and their co-workers observed that bibenzyls and pinacols are oxidatively cleaved upon irradiation in the presence of NDN.[11] No quantum yields were reported but flash photolysis experiments revealed that for pinacols and one of the bibenzyls, benzyl radicals are formed. We attributed the reaction in degassed medium to attack of the benzyl radicals on NDN, the radical anion $NDN^{-\bullet}$ or the naphthyl radical $NDNH^{\bullet}$. Thus, investigation of the reaction of the substrates in the presence and in the absence of oxygen in order to understand the role of radicals under these conditions is discussed.

Results and Discussion

Irradiation of 2×10^{-2}M toluene or 1,2,4,5-tetramethylbenzene (**1a, b**) in oxygen-saturated acetonitrile solution in the presence of 1×10^{-4}M-NDN (light is absorbed by the latter) leads to the oxidation of the methylbenzenes to give the corresponding aldehydes (**2**) (Scheme 1). Under these conditions NDN is virtually unchanged even after several mol of the methylbenzenes per mol of NDN are oxidized. With a lower oxygen concentration, *e.g.* in air- rather than oxygen-equilibrated solution, some NDN is consumed (to yield the previously reported[9] adduct with the methylbenzenes) and a minor amount of the alcohol (**3b**) is obtained along with the corresponding aldehyde.

Under these conditions the bibenzyls (**4a**) and (**4b**) are oxidatively cleaved to the corresponding benzaldehydes (**5**), and compounds (**4c, d**) yield a mixture of phenyl ketones (**5**) and benzyl alcohols (**6**). Again NDN is not consumed and formation of the adducts obtained in the absence of oxygen[9] is suppressed. In air-equilibrated solution some diphenylmethane is formed from tetraphenylethane (**4c**) along with the oxidation product. Oxidative cleavage is also observed for the aromatic pinacols (**7a—c**) with formation of the corresponding ketones or aldehydes. NDN, which is reduced in the absence of oxygen, is not affected under these conditions [or only slightly in the case of compounds (**7b, c**)]. Pinacol ethers (**9b, c**) give a mixture of the corresponding ketone or aldehyde and methyl benzoate, and none of the reduced NDN and NDN adducts are found in the absence of oxygen.

Oxidation of some of these donors has been previously considered by Griffin and Das [bibenzyls (**4b—d**), pinacols (**7a, b**), and pinacol ether (**9b**)][11a] and the results are qualitatively the same. However, in our case conversion was kept low in order to avoid photochemical reaction of the products, which absorb significantly at the irradiation wavelength, and thus interfere with the NDN-initiated photoreaction. As NDN is not consumed under these conditions, it can be considered to act as a sensitizer and several mol of substrate can be converted per mol of NDN, although the rate of the reaction is constantly reduced due to absorption by the products.

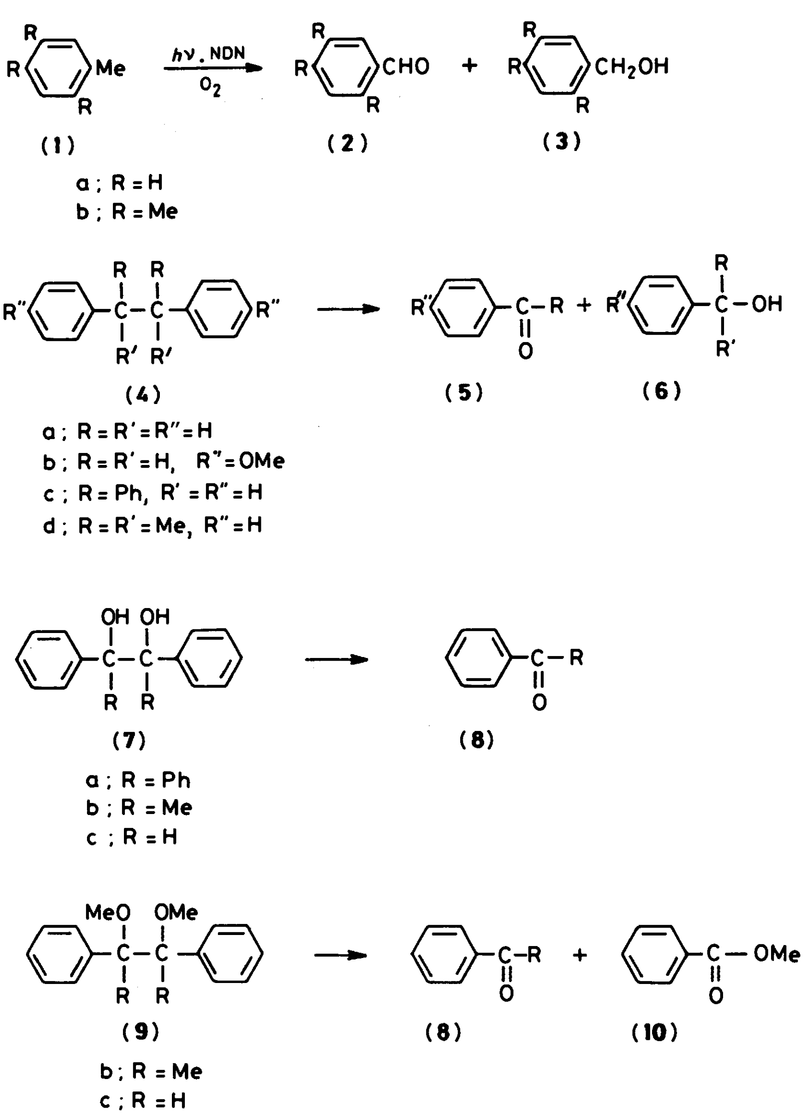
Products obtained in oxygen-saturated solution and their quantum yield of formation are compared in Table 1 with quenching constants of NDN fluorescence by the substrates, and with products formed and quantum yield (refers to NDN consumption) for the reaction in the absence of oxygen at the same substrate concentration. This comparison allows some mechanistic conclusions to be deduced.

The reaction involves charge-transfer interaction between the substrates and the singlet excited state of NDN since (i) no reaction occurs in the absence of NDN; (ii) oxidation of the substrates in benzene is much slower than in polar acetonitrile [*e.g.*, quantum yield of (**7a**) in benzene is *ca.* 11% of that for (**7a**) in acetonitrile). Similarly, 1% for (**1b**) in benzene compared with acetonitrile as solvent, and even less for (**4d**)]; (iii) all of the substrates quench the fluorescence of NDN according to the Weller equation[12] and electron-transfer to NDN singlet excited state (not to the triplet) is feasible; (iv) in the absence of oxygen the photochemical reaction between NDN and the substrates has been shown to involve charge-transfer.[8,9,13]

Thus, the radical ion pair formed according to equation (1) originates both in the presence and in the absence of oxygen (DH = donor).

$$NDN^{1*} + DH \rightleftharpoons (NDN^{-\bullet}DH^{+\bullet}) \qquad (1)$$

Distinction between the two main pathways, *viz.* activation of oxygen by electron-transfer and subsequent reaction of the



Scheme 1.

superoxide anion with the donor radical cation [equations (2) and (3)] [electron-transfer according to equation (2) is largely

$$NDN^{-\cdot} + O_2 \longrightarrow NDN + O_2^{-\cdot} \qquad (2)$$

$$DH^{+\cdot} + O_2^{-\cdot} \longrightarrow \text{Products} \qquad (3)$$

exothermic[14a]] or photosensitized formation of benzyl radicals by proton transfer, or carbon–carbon bond cleavage in the bibenzyls, followed by reaction of these species with (presumably ground state) oxygen, can be deduced from

$$(NDN^{-\cdot}\, DH^{+\cdot}) \longrightarrow \text{Benzyl radicals} \xrightarrow{O_2} \text{Products} \qquad (4)$$

comparison of the reactions in the presence and in the absence of oxygen and from fluorescence lifetime and flash photolysis measurements. The data in Table 1 were obtained with a 0.02M substrate concentration. Under these conditions quantum yields approach the limiting value and quenching of singlet NDN by oxygen is much lower than substrate quenching, so that a quantitative comparison can be made.

The stoicheiometry of the reaction with the pinacols in the absence of oxygen may be given as:

$$NDN + PhRC(OH)CPhROH \xrightarrow{h\nu} NDNH_2 + 2PhRCO \qquad (5)$$

and in the presence of oxygen as:

$$PhRC(OH)CPhROH \xrightarrow{NDN,\, h\nu} 2PhRCO + H_2O \qquad (6)$$

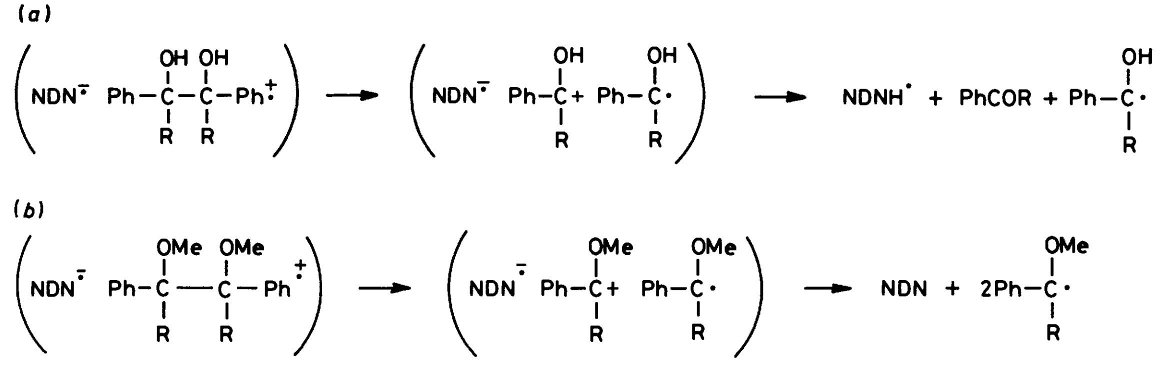
Quantum yield for ketone (or aldehyde) formation in the presence of oxygen [calculated according to equation (6), 2 mol of ketone per absorbed quantum] is only slightly larger than in the absence of oxygen. Thus the reaction is the same in both cases and the determining step is not reaction with oxygen but carbon–carbon bond cleavage in the radical cation and proton transfer from the benzylic cation to $NDN^{-\cdot}$ (see Scheme 2*a*). In the presence of oxygen the naphthyl radical is reoxidized to NDN and the benzyl radical yields the ketone, otherwise hydrogen-transfer leads to the results reported in equation (5). In accord with this result, Das has found by nanosecond flash photolysis the presence of benzyl radicals from (**7a**, **b**) and (**9b**) immediately after the flash, as well as in their reaction with oxygen.[11a]

With pinacol ethers (**9**), comparison of quantum yields shows

Table 1. Products and quantum yield for the reaction of substrates (**1**), (**4**), (**7**), and (**9**) upon irradiation in the presence of NDN[a]

Substrate	Oxygen-saturated solution product (quantum yield)[b]	Deoxygenated solution k_{et}/M^{-1} s^{-1}	Deoxygenated solution Product (quantum yield)	Φ'/Φ[c]
(**1a**)	ArCHO (0.014)	0.19×10^{10}	Adduct with $ArCH_2$ (0.012)[d]	1.2
(**1b**)	ArCHO (0.1)	1.63	Adduct with $ArCH_2$ (0.03)[d]	3.3
(**4a**)	ArCHO (0.012)	0.18	Adduct with $ArCHCH_2Ar$ (0.075)	0.16
(**4b**)	ArCHO (0.02)	1.95	Adduct with $ArCHCH_2Ar$ (0.017)	1.2
(**4c**)	ArCOR (0.02), ArCRR'OH (0.035)	1.25	Adduct with ArCRR'' (0.012)	4.6
(**4d**)	ArCOR (0.023), ArCRR'OH (0.009)	0.99	Adduct with ArCRR'' (0.018)	1.8
(**7a**)	ArCOR (0.125)	1.24	$NDNH_2$ + ArCOR (0.14)	0.9
(**7b**)	ArCOR (0.025)	1.01	$NDNH_2$ + ArCOR (0.025)	1
(**7c**)	ArCOR (0.008)	0.97	$NDNH_2$ + ArCOR (0.008)	1
(**9b**)[d]	ArCOR (0.025), $ArCO_2Me$ (0.02)	0.66	$NDNH_2$ + ArCOR + adduct with ArRCOMe (0.02)	1.1
(**9c**)	ArCOR (0.0002), $ArCO_2Me$ (0.004)	0.24	$NDNH_2$ + ArCOR + adduct with ArRCOMe (0.005)	0.85

[a] Substrate concentration 0.02M for the reaction in deoxygenated solution, see references 8*b*, 9, and 10. [b] Yield is calculated taking into account that oxidative cleavage of the substrate yields 2 mol of products, according to equation (6). [c] Ratio between quantum yield in the presence (Φ') and in the absence of oxygen (Φ). [d] Substrate concentration 0.005M.

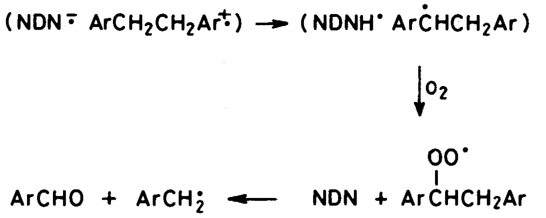


Scheme 2.

that the reaction is again the same in the presence of oxygen.* The methoxy benzyl cation is reduced by $NDN^{-\bullet}$ to the corresponding radical and reaction with oxygen yields peroxy radicals which decompose to give a mixture of ketones (or aldehydes) and esters (see Scheme 2*b*).

In the case of bibenzyls two different situations arise. Compounds (**4c, d**) undergo carbon–carbon bond cleavage both in the absence and in the presence of oxygen, but the quantum yield is much higher in the latter case. Furthermore, formation of diphenylmethyl radicals from (**4c**) has been demonstrated by flash photolysis.[11a] Cleavage of the radical cation may occur in a manner analogous to Scheme 2*b*. In the absence of oxygen benzyl radicals in part react with NDN to give adducts, and in part recombine to give the starting bibenzyl. Oxygen intercepts the benzyl radicals more efficiently than NDN does, to give peroxy radicals and hence the observed ketones and alcohols.

In contrast to (**4c, d**), bibenzyls (**4a**) and (**4b**) are not cleaved by photoexcited NDN in the absence of oxygen, and addition between NDN and the bibenzyl radicals is observed. In oxygenated solution carbon–carbon bond cleavage does take place. Quantum yield is lower than or near to the value of photoaddition in degassed solvent for (**4a**) and (**4b**) respectively. The chemistry observed can be rationalized through deprotonation of the radical cation as in deaerated solution, reaction of the benzyl radical with oxygen, and carbon–carbon bond cleavage in the peroxyl radical (Scheme 3), a mechanism analogous to the auto-oxidation of these substrates.[14b] Thus the extra stabilization of benzyl radicals from (**4c, d**) makes fragmentation of these substrates feasible, whereas for (**4a, b**) this is only possible through the indirect pathway shown in Scheme 3.



Scheme 3.

Oxidation of the methylbenzenes to give the corresponding aldehydes is as efficient as the anaerobic photoaddition of NDN

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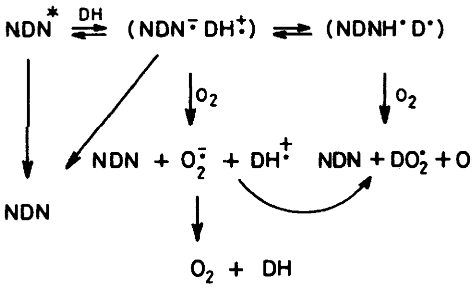
* This supports the hypothesis that carbon–carbon bond cleavage precedes proton transfer for pinacol and pinacol ethers, as reported in Scheme 2, in contrast to the alternative mechanism reported in equations (7) and (8).

$$[NDN^{-\bullet}PhRC(OH)CPhROH^{+\bullet}] \longrightarrow NDNH^{\bullet} + PhRC(O^{\bullet})CPhROH \quad (7)$$

$$PhRC(O^{\bullet})CPhROH \longrightarrow PhRCO + PhR\dot{C}OH \quad (8)$$



Scheme 4.

and toluene and more efficient than that of 1,2,4,5-tetramethylbenzene. A distinctive feature of the photo-oxidation of the less reactive bibenzyls (**4a**, **b**) and of the methylbenzenes is their dependence on oxygen pressure, *i.e.* the reaction is much slower in air- than in oxygen-equilibrated solution. Correspondingly, only the donor radical cations and no benzyl radicals were detected by flash photolysis [as seen for (**4b**) 1,2-bis(methoxyphenyl)ethane and *p*-xylene[11a]]. Thus benzyl radicals formed, as demonstrated by the products obtained, are not sufficiently stable to diffuse out of the radical cage and oxygen quenches either the excited donor–acceptor complex or the radical pair (Scheme 4), both shorter-lived species than the previously considered stable radicals.

The situation is complicated by the reversibility of some of the reactions involved. Indeed, fluorescence lifetime measurements in the presence of toluene show that quenching of the NDN singlet excited state occurs at a much higher rate than deduced by steady-state measurements, and furthermore that it is reversible.† From previous evidence[9] we also think that proton transfer within the excited complex is reversible. Unambiguous definition of the mechanism is difficult due to the several possibilities available. However, that oxygenation involves the same sequence as anaerobic photoaddition is indicated not only by the kinetic evidence below, but by the parallel quenching of both reactions by good donors, such as 1,4-dimethoxybenzene at concentrations low enough to avoid quenching of NDN^{1*}.

In selected cases, quantum yield measurements were extended to different substrate concentrations. The minimum kinetic scheme, disregarding the mechanism of reaction of the radical ion pair, of which only the partitioning towards reaction and unproductive decay is considered, is:

$$NDN^{1*} \xrightarrow{k_d} NDN$$

$$NDN^{1*} + DH \xrightarrow{k_{et}} (NDN^{-\cdot}DH^{+\cdot})$$

$$NDN^{1*} + O_2 \xrightarrow{k'_d} NDN + O_2$$

$$(NDN^{-\cdot}DH^{+\cdot}) \xrightarrow{k_{-et}} NDN + DH$$

$$(NDN^{-\cdot}DH^{+\cdot}) \xrightarrow{k_r} \text{Products}$$

$$(NDN^{-\cdot}DH^{+\cdot}) + O_2 \xrightarrow{k'_r} \text{Products}$$

The quantum yield for reaction in the absence (Φ) and in the presence of oxygen (Φ') are expressed by equations (9) and (10).

Table 2. Parameters for the reaction of substrates (**4a**), (**4c**), and (**7a**)

	Oxygen-saturated solution			Deoxygenated solution		
Substrate	K'_{sv}/M^{-1} [a]	K'_{sv}/M^{-1} [b]	Φ'_{lim}	K_{sv}/M^{-1} [a]	K_{sv}/M^{-1} [b]	Φ'_{lim} [c]
(**4a**)	7	8	0.85	18.5	21.5	0.25
(**4c**)	48	36	0.18	125	128	0.021
(**7a**)	47	31	0.3	124	120	0.22

[a] Calculated from fluorescence quenching measurements. [b] Calculated from the doubly reciprocal plot Φ^{-1} *vs.* $[D]^{-1}$ (see Figure 1). [c] Limiting quantum yield at infinite donor concentration (see Figure).

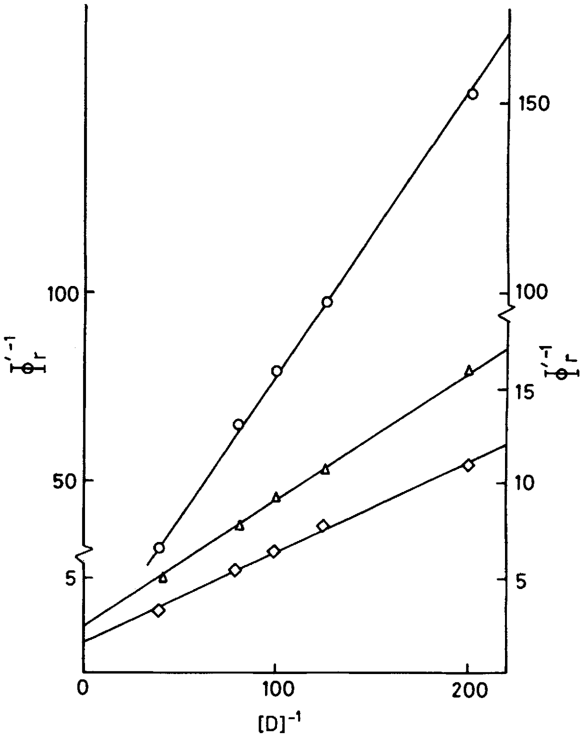


Figure. Double reciprocal plot for reaction quantum yield (Φ_r') *vs.* donor concentration for the NDN-sensitized oxidation of bibenzyl (**4a**) (○), 1,1,2,2-tetraphenylethane (**4c**) (△), and 1,1,2,2-tetraphenylethane-1,2-diol (**7a**) (◇)

A double reciprocal plot of reaction quantum yield *vs.* donor concentration is linear both in the absence and with a fixed

$$\Phi = \frac{k_{et}[DH]}{k_d + k_{et}[DH]} \times \frac{k_r}{k'_d + k_{-et} + k_r} \tag{9}$$

$$\Phi' = \frac{k_{et}[DH]}{k_d + k'_d[O_2] + k_{et}[DH]} \times \frac{k_r + k'_r[O_2]}{k'_d + k_{-et} + k_r + k'_r[O_2]} \tag{10}$$

concentration of oxygen. The ratio intercept/slope corresponds in both cases to the Stern–Volmer constant for quenching of the NDN singlet state, $K_{sv} = k_{et}/k_d$ and $K'_{sv} = k_{et}/(k_d + k'_d[O_2])$ respectively, a quantity which can also be measured from the fluorescence quenching in the absence and at the same concentration of oxygen respectively. The Figure and Table 2

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† A preliminary study by Dr. Masetti (Perugia) shows that quenching of singlet excited NDN by toluene in MeCN follows a complex behaviour. The excited complex releases NDN^{1*} and furthermore is itself quenched by toluene. For related studies of the NDN–methylbenzenes system in apolar solvents, see H. F. Davis, S. K. Chattopadhyay, and P. K. Das, *J. Phys. Chem.*, 1984, **88**, 2798.

show that this analysis holds and yields a quantitative support to the proposed mechanism. For compounds (**4c**) and (**7a**), k'_{sv} evaluated from the reaction quantum yield measurements is lower than the value obtained from fluorescence quenching. The quantum yield, Φ', decreases less than expected at low donor concentration. This is probably due to reaction of oxygen with benzylic radicals of enhanced stabilization present in these cases which would otherwise recombine to give the starting material.

It has been reported that no cross coupling of benzyl radicals occurs when a mixture of 1,2-bis-(*p*-methylphenyl)ethane, 1,2-bis-(*p*-methoxyphenyl)ethane, and NDN is irradiated in the absence of oxygen.[11a] Indeed, we have shown that these bibenzyls [as opposed to bibenzyls with a weaker carbon–carbon bond, such as (**4c**, **d**)] do not fragment in the absence, but only in the presence of oxygen. In contrast, stabilized radicals readily escape from the radical cage, are detected by flash photolysis and, in the absence of oxygen, yield a cross coupling product [*e.g.*. epimerization of *rac*-2,3-dimethoxy-2,3-diphenylbutane to the *meso* isomer (**9b**)].[11a]

Experimental

Naphthalene-1,4-dicarbonitrile was prepared and purified as previously described.[15] Spectrograde solvents (acetonitrile and benzene) were used as received. Toluene, 1,2,4,5-tetramethylbenzene, and bibenzyl were commercial product and were purified by fractional distillation or recrystallization. 1,2-Bis-(*p*-methoxyphenyl)ethane (**4b**) was prepared according to the method by Trahanosky[16] and purified by chromatography on alumina and recrystallization from cyclohexane. 1,1,2,2-Tetraphenylethane (**4c**) was prepared according to the method by Gilman[17] and recrystallized from acetic acid. 2,3-Dimethyl-2,3-diphenylbutane (**4d**) was prepared by the Wurz procedure[18] and recrystallized from ethanol. 1,1,2,2-Tetraphenylethane-1,2-diol (**7a**) was prepared by photochemical reduction of benzophenone,[19] 2,3-diphenylbutane-2,3-diol (**7b**) by Grignard reaction of benzil and methyl iodide,[20] and 1,2-diphenylethane-1,2-diol (**7c**) by Al amalgam reduction of benzil.[21] The pinacol ethers (**9b**) and (**9c**) were prepared from the corresponding pinacols according to reference 11*a*.

Photochemical Reactions.—Photochemical reaction of oxygen-purged solutions were carried out either in serum capped Pyrex tubes arranged in a merry-go-round and irradiated in an Applied Photophysics multilamp apparatus fitted with 310 nm fluorescent lamps or in 1 cm spectrophotometric cells on an optical bench and irradiated by means of light from a super-high-pressure Osram 200 W/2 mercury arc focalized and monochromatized through an interference filter (313 ± 5 nm). Products were identified by comparison with authentic samples and quantitatively determined by either g.l.c. (Hewlett Packard 5100 A apparatus SP 2100 3% or Carbowax 20M 5% columns) or h.p.l.c. (Waters apparatus, Corasil column, ethyl acetate–cyclohexane mixtures as eluants). NDN consumption was checked by absorption spectroscopy. Light flux ($1-3 \times 10^{-7}$ einstein min^{-1} cm^{-2}) was measured by ferrioxalate actinometry.

Fluorescence Quenching.—Fluorescence intensities were measured by means of an Aminico Bowman MPF spectrophotometer in 1 cm spectrophotometric cells after either freeze-degas-thaw degassing or oxygen purging. Linear Stern–Volmer plots for a quenching of NDN fluoresence were obtained in each case.

Acknowledgements

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