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The Photochemical Reaction between 1,4-Dicyanonaphthalene and Benzyl Ethers

Nicola d'Alessandro, Mariella Mella, Elisa Fasani, Lucio Toma, and Angelo Albini

Dip. Chimica Organica, Università, V. Taramelli 10 I-27100 Pavia, Italy

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Key Words: Photochemical electron transfer; Benzyl ethers radical cations; Dicyanonaphthalene stereoselective photoadditions;

Abstract *- Irradiation of 1,4-dicyanonaphthalene (DCN) and benzyl methyl ether gives the two diastereoisomeric 1-substituted 1,2-dihydronaphthalenes. A stereochemical assignment for these products, and related diastereoisomers pairs is proposed. The reaction occurs via the free radical ions and the low quantum efficiency is due to the slow deprotonation of the radical cation, with only moderate salt effect. In accordance with this scheme, the reaction with benzyl ℓ-menthyl ether gives a low enantiomeric eccess.*

Photochemical hydrogen transfer from alkyl aromatics occurs by either of the two mechanisms, viz. homolytic hydrogen abstraction (e.g. with the $n\pi^*$ triplet state of ketones)[1-5] or electron transfer and proton transfer (with good electron acceptors such as the $\pi\pi^*$ triplet of some ketones [1-6] and the excited singlet of some aromatics)[6-8]. The detailed mechanism and stereochemical implication of these reactions have been extensively investigated. However, in contrast with the variety of excited states used as acceptors, only a limited choice of substrates has been considered as donors, and the effect of α substituents in the chain has been disregarded. We presently report results about the reaction between benzyl ethers and photoexcited 1,4-dicyanonaphthalene as a first effort toward the overcoming of these limitations.

RESULTS

Reaction with benzyl methyl ether. The fluorescence of 1,4-dicyanonaphthalene (DCN) is quenched by benzyl methyl ether (**1a**, Stern Volmer constant, K_{sv} 3.5 M^{-1} in acetonitrile), and DCN is slowly consumed (quantum yield < 0.01) when irradiated in the presence of 0.3 M **1a** in deaerated acetonitrile. The products formed, besides some of the corresponding pinacol dimethyl ether and 1,2-dihydro-1,4-dicyanonaphthalene

3a, clearly recognized on the basis of their spectroscopic and analytic properties (see Tables 1 and 2, and Experimental Section). In our preliminary investigation[9] one of the isomers seemed to be formed in overwhelming amount, but the present experiments show that the yields are similar.

Scheme I

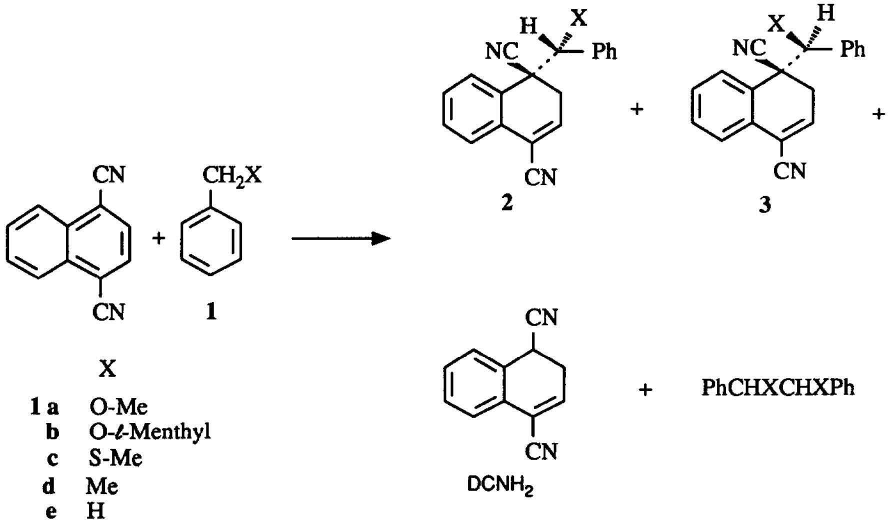


Table 1. Products for the Irradiation of 1,4-Dicyanonaphthalene (DCN) and Benzyl Ethers in Deareated Acetonitrile

Ether	Conditions	Adducts (% Yield)
1a	MeCN, anhydrous, 30 h	**2a**(18), **3a**(30)[a]
1a	MeCN, 0.1% H_2O, 16 h	**2a**(30), **3a**(37)[a]
1a	MeCN, 0.1 M $LiClO_4$, 6 h	**2a**(34), **3a**(50)[a]
1a	MeCN, 0.1% H_2O, 3 h	**2b**(20), **2'b**(13), **3b**(21), **3'b**(15)

a : Other product are benzaldeyde, 2,3-dimethoxy-2,3-diphenylbutane and 1,2-dihydro-1,4-dicyanonaphthalene

Stereochemical assignment. Since we obtained a number of diastereoisomeric 1-substituted 1,2-dihydronaphtalenes of the type **2a**/**3a** in the course of this work (see also below) and of other investigations,[10,11] the series was examined in view of stereochemical assignments based on NMR spectra (see Table 2) and molecular mechanics calculations. Conformational analysis was performed on model isomeric (*RR*)/(*SS*), **4**, and (*RS*)/(*SR*), **5**, compounds as it is expected that the cyano substituent on C(4) could exert no significant influence on the conformational behaviour of the molecules.

Compounds **4** and **5** can assume different conformations as a consequence of a) inversion of the cyclohexadiene ring from half-chair $^2H_1$ to half-chair $^1H_2$; such an operation exchanges the orientation of the two substituents at C(1) from pseudo axial to pseudo equatorial and vice versa; b) rotation around the C(1)-Cα

Table 2. ^{1}H NMR Absorptions for the 1-Alkyl-1,4-dicyano-1,2- dihydronaphthalenes **2** and **3**

Compound	X	H-2a(Δδ)^b	H-2b(Δδ)	=CH	PhCH	$J_{2a,2b}$	$J_{2a,3}$	$J_{2b,3}$
2a	OMe	2.82(0.8)	2.75(0.8)	6.52	4.20	19	6.6	3
3	OMe	3.62(0.6)	3.00(0.85)	6.90	4.20	19	6.8	2.7
		H-2a	H-2b	=CH	PhCH			
2b	O-Menthyl	2.78	2.7	6.6	4.45			
2'b	O-Menthyl	3.08	3.0	6.55	4.45			
3b	O-Menthyl	3.65	2.95	6.8	4.55			
3'b	O-Menthyl	3.55	2.95	6.8	4.3			
2c	SMe	2.82	2.75	6.6	3.85			
3c	SMe	3.80	3.05	6.9	3.9			
2d	Me	3.12	3.0	6.6	3.0			
3d	Me	2.85	2.55	6.7	3.05			
2e≡3e	H	2.98	2.9	6.8	2.9			

a : In $CDCl_3$ b : Δδ · upfield shift is going from $CDCl_3$ to C_6D_6

single bond; c) rotation around the Cα-O single bond. So, in principle, 18 local minima are expected for each compound and the number might be even higher if rotation of the phenyl group produces more than one not degenerated minimum.

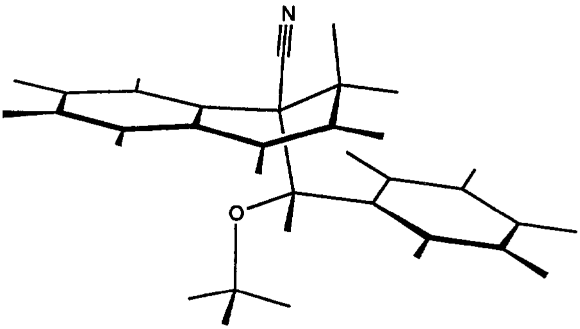
When the conformational space of **4** and **5** was explored through Allinger's MM2(85) program,[12] 12 and 13 local minima were, respectively, located. Table 3 reports selected geometrical data for the conformers which give a non negligible contribution to the overall population. In both cases three low energy minima were found close to global minimum. Moreover, in both cases the cyclohexadiene ring preferentially assumes the $^2H_1$ conformation [conformers **4A**, **4B**, **4D** and **5A**, **5B**, **5C**; (8a-1-2-3) 45°] having the cyano group in the pseudo-equatorial and the other large substituent in the pseudo-axial orientation with an almost free rotation around the C(1)-Cα bond [see (8a-1-Cα-Cβ)]. On the contrary, when the cyclohexadiene ring assumes the $^1H_2$ conformation (**4C** and **5D**) rotation around C(1)-Cα is not easy. Though qualitatively similar, the two sets of conformers **4A-D** and **5A-D** differ in the distribution of the energies: in the former case energies are grouped in a range of only 0.24 kcal/mol while in the latter they are more spread. So, while in the (*RR*)/(*SS*) isomer **4** the two half-chair conformations are both populated (73%-27%), in the (*RS*)/(*SR*) isomer **5** half-chair $^2H_1$ is strongly favored.

Correspondly, in one of the products the two hydrogens in position 2 of the naphtalene ring resonate very close one to the other, while in its isomer one of the two protons is strongly deshielded. It is difficult to predict from the models the chemical shifts of these protons since it can be a priori influenced by several factors such as the conformation of the cyclohexadiene ring, the relative position and orientation of the cyano group at C(1) and of the phenyl group. However, the fact that the differentiation of the protons is observed only when there is a bulky group in α (-OR, -SR, much less with -Me), as well as the reduced shift in going from $CDCl_3$ to C_6D_6 as the solvent (Δδ, Table 2), identify the downfield signal as the endo proton (see

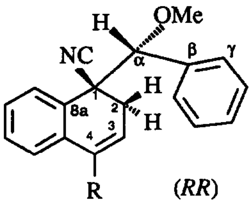
Table 3. Relative energies (kcal/mol), equilibrium percentages (25 °C) and selected geometrical data for conformations of compounds **4** and **5**.

Conf	E_{rel}	equil percent	torsional angles			
			8a-1-2-3	8a-1-Cα-Cβ	1-Cα-O-Me	Ha-Cα-Cβ-Cγ
4A	0.00[a]	27.6	+50	+54	+170	+19
4B	0.01	27.0	+44	-65	+176	+20
4C	0.02	26.9	-46	+180	+165	+28
4D	0.24	18.5	+47	+176	+166	+26
5A	0.00	81.2	+51	-175	-169	-18
5B	1.22	10.3	+42	-60	-166	-26
5C	1.64	5.1	+46	+61	-168	-24
5D	1.88	3.4	-50	-162	-167	-12

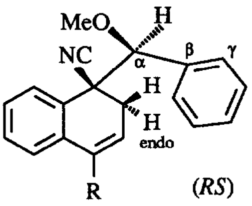
a : 0.83 Kcal / mol relative to 5A



5 A



2a : R = CN
4 : R = H



3a : R = CN
5 : R = H

figure). Despite the above mentioned uncertainty about the origin of such shift, it is likely that any differentiation appears in the conformationally fixed rather than in the more equilibrated isomer, and therefore we propose that **2a** is the (*RR*)/(*SS*) isomer and this applies to the related derivatives.

Dependence on experimental conditions. The effect of experimental parameters both on the reaction rate and on the product distribution was examined. Thus, in contrast with the reaction in MeCN, virtually no change occurs on prolonged irradiation of DCN and **1a** in either dichloromethane or cyclohexane, although the fluorescence of the nitrile is quenched also in this case (K_{sv} is again 3.5 M^{-1}).

Small additions of protic solvents increase the rate of reaction. Thus, product formation is faster (Φ_{rel} 2) in acetonitrile containing 0.1% in volume of either water or methanol as compared to the reaction in anhydrous solvent, and the **2a**/**3a** ratio changes somewhat (Table I).

The rate is also increased by the additions of tetrabutylammonium perchlorate, and, more markedly, lithium perchlorate (Φ_{rel} 4), but the product ratio is scarcely affected in both cases. On the contrary, the reaction is almost completely quenched by tetrabutylammonium chloride.

Reaction with benzyl ℓ-menthyl ether. In order to explore the possible influence of a neighboring chiral centre on the formation of the new carbon-carbon bond, the irradiation of DCN was carried out using benzyl ℓ-menthyl ether as the substrate. The scope of this reaction is exactly the same as with **1a**, with exclusive attack at the benzylic group and no competitive hydrogen abstraction from the menthyl moiety (recovered **1b** is unchanged in its spectroscopic properties, including α_D). Thus, the products formed are again 1 substituted 1,2-dihydronaphthalenes. Due to the presence of additional chiral centers, four diastereoisomers are expected and indeed are obtained. Two of them (**2b** and **3b**) were isolated in the pure state through repeated chromatography and recrystallisation, while for the other ones (**2'b** and **3'b**) only incomplete purification was obtained. However, the ABX absorption on the NMR spectrum of compounds **2b** and **2'b** on one hand, and **3b** and **3'b** on the other one, closely fitted in the pattern discussed above (see Table 2) and assured of the configuration across the naphthyl-benzyl bond. The ratio of the isomers is 1.55 for the **2b**/**2'b** pair and 1.4 for the **3b**/**3'b** pair, with total **2**/**3** ratio very near to one.

DISCUSSION

Hydrogen abstraction from the benzyl ethers clearly takes place through the electron transfer-proton transfer sequence. The radical cations of donors **1** are intermediates in the reaction as shown by the quenching of the DCN fluorescence and the requirement of polar solvents. Benzyl radical cations are known as strong acid.[16] Thus in the case of toluene a largely negative ΔH (= -17 kcal M^{-1}) has been calculated for deprotonation (eq. 1), on the basis of the measured oxydation potential of the benzyl radical[17].

$$PhCH_3^{\cdot +} \longrightarrow PhCH_2^{\cdot} + H^+ \qquad (1)$$

In the ethers **1**, to a slight stabilization of the radical cation corresponds a more marked stabilization of the radical, and thus the process of eq. 2 is expected to be thermodynamically even more favoured as compared to eq. 1.

$$PhCH_2OR^{\cdot +} \longrightarrow Ph\dot{C}HOR + H^+ \qquad (2)$$

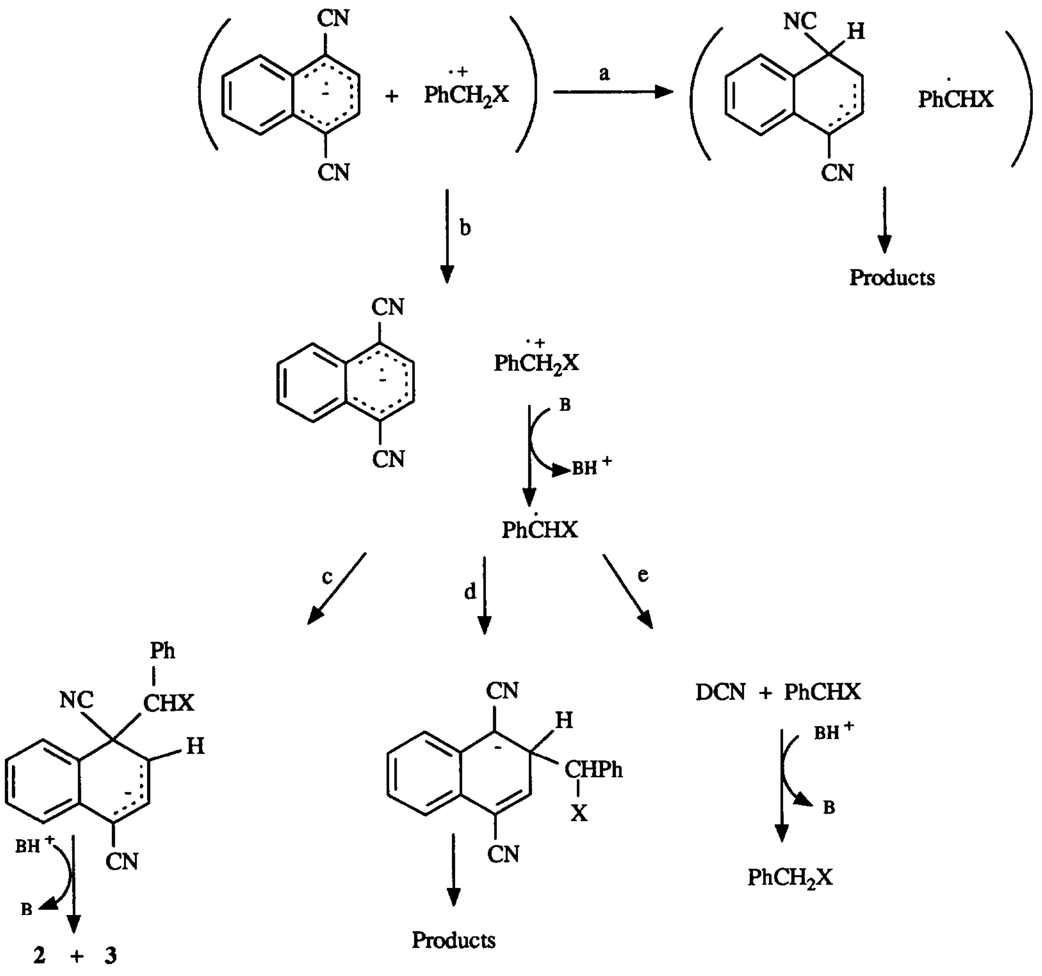
However, the observed reaction is slow and actually less efficient than for the system DCN-toluene despite the fact that > 50% of DCN excited singlet is quenched under the reaction conditions. This requires that the fate of radical ions is back electron transfer (eq. 3, expected to occours at a rate of ca $5x10^9$ M^{-1} s^{-1}

from the analogy with similar systems)[18] rather than chemical reaction (to yield neutral radicals, eq. 2, and hence adducts or products from homo coupling, such as pinacol ethers).

$$DCN^{-} + PhCH_2OR^{\cdot+} \longrightarrow DCN + PhCH_2OR \qquad (3)$$

Apparently, the limiting factor is the absence of a convenient base, and this makes proton transfer a kinetically insignificant, if thermodynamically favoured, process.

Scheme II



More precise mechanistic conclusions can be drawn with reference to previous investigations of the DCN-alkylbenzenes system.[10,19] These led to the distinction of two processes after initial electron transfer to singlet excited DCN, viz proton transfer within the solvent cage, followed by addition of the two neutral radicals (path a is Scheme II), and diffusion of the two radical ions, followed by deprotonation of the free radical cation and radical-radical anion combination (path b). The former path leads to formation of a new cycle, the latter one gives alkylated (in position 1 and 2, paths c and d) 1,2-dihydronaphthalenes, usually with low quantum yield (while path a reaches $\Phi \sim 0.3$ in some cases).[8,9]

The present reaction clearly fits in the latter class, as far as both product distribution and efficiency are concerned. This is rationalized on two grounds. First, the ionization potential of ethers is near to that of alkylbenzenes (e.g. the IPs for methyl ethyl ether and benzylchloride, reasonable models for the two moieties in ethers **1** are 9.86 and 9.29 eV respectively)[20] and a structure with the charge localized on the oxygen atom is expected to contribute heavily to the radical cation structure. This is expected to favour better solvation and hence diffusion of the radical ions against in cage proton transfer, since the latter apparently occurs only for a particular conformation of the initial pair.[10,19]

In accordance with this, the two possible stereoisomers **2** and **3** are formed in similar amount and the influence of a pre-existing chiral group on the stereochemistry of the new centers is limited (see the experiments with **1b**) while, in view of the conformational requirements for proton transfer (the C-H bond has to be aligned with the π cloud in the radical cation) a greater effect would be expected, would the entire sequence proton transfer - carbon-carbon bond formation take place within the solvent cage. Stabilization of the radical ions by additions of salts, or making deprotonation easier with small amount of additives, such as water or methanol, which offer an alternative proton acceptor, have a beneficial effect on the quantum yield, but this is limited in view of the high rate of back electron transfer.

A second limitation to the formation of adducts stems from the fact that, even if the radicals are formed, the presence of the alkoxy group makes their reduction potential much less negative than for unsubstituted benzyl radicals and hence encounter with DCN^{-} does not necessarily lead to combination, but may as well involve electron transfer ($E_{1/2}^{red}$ is -1.28 for DCN and around -1.3 V vs SCE for the diethyl ether radical)[21] and reprotonation of the benzyl anion, and thus, again, no net chemical change (path e rather than path c in Scheme II). Finally we note that chloride ions completely suppresses the reaction; under this condition ion recombination takes place with intersystem crossing to the lowest lying triplet (in this case the unreactive DCN^{3*}). There is a precedent for such on effect.[22]

CONCLUSION

This work emphasizes some of the limitation intrinsic to deprotonation reactions following photochemically induced electron transfer. Radical cations have usually available favourable fragmentation pathways, e.g. benzyl radical cation are thermodynamically strong carbon acids. However, overcoming the kinetic inefficience of the process is not simple. Thus, introducing an alkoxy group, while both decreasing the C-H bond dissociation energy and favouring separation and diffusion of the radical ions, has no beneficial effect since it does not overcome the limiting factor, the slow deprotonation, and furthermore introduces a new factor of inefficiency, path e. Attention to such factors must be paid in looking for a strategy for overcoming the usual low efficiency of electron-transfer photochemical reaction,[23] a task that has proven difficult, so that no general solution has been provided up to now. The strategy has to be different, at any rate, when fragmentation of a σ bonds in radical cations of alkyl derivatives is involved, as compared to the addition reactions usually observed with the relatively more stable alkene radical cations.

EXPERIMENTAL

Anhydrous acetonitrile was obtained by refluxing and distilling over CaH_2. 1,4-Dicyanonaphthalene was prepared and purified as previously described.[13] Benzyl methyl ether[14] and benzyl ℓ-menthyl ether [15] were obtained according to literature procedures.

Photochemical reaction between DCN and ***1a***. A solution of DCN (200 mg) and **1a** (4.5 mL) in 130 mL acetonitrile (containing 0.1% water) was deaerated by bringing to boil and cooling under argon, and then irradiated at 17°C by means of a 125 W Philips HPK high pressure mercury arc through Pyrex while maintaining a slow purging with argon. After 16 h tlc revealed that most of DCN had been consumed. Evaporation of the solvent under reduced pressure and column chromatography of the residue on silica gel eluting first with cyclohexane and then cyclohexane-ethyl acetate mixtures (from 9 to 1 to 7 to 3), followed by further chromatography of the fractions containing the adducts on silica gel plate eluting with cyclohexane-ethyl acetate 8 to 2 gave products: **2a**, 93 mg (30%), colourless needles from MeOH, mp 143-5°C, analysis, found. C, 79.65; H, 5.45; N, 9.12% calculated for $C_{20}H_{16}N_2O$: C, 79.98; H, 5.37; N 9.33. **3a**, 115 mg (37%) colourless needles from MeOH, m.p. 149-51°C, analysis, found, C, 79.80; H 5.25; N, 9.15.

Photochemical reaction between DCN and ***1b***. A solution of DCN (200 mg) and **1b** (1.5 mL) in 130 mL acetonitrile was deaerated and irradiated as above for 3 h. Chromatography as above gave two fractions, the first eluting containing **3b** and **3'b** (102 mg) and the latter **2b** and **2'b** (97 mg) (note the inversion in the eluting order with respect to the **2a**-**3a** system). Quantitative evaluation of the isomers within each pair (see Table 1) was accomplished by NMR (in the presence of $Eu(FOD)_3$ in the case of compounds **2b**-**2'b**, since the resonances were otherwise not sufficiently separated). A second plate chromatography of each fraction followed by recrystallization of the upper part of the band from methanol gave in each case the main isomer almost pure, though in small amounts: **2b**, colourless needles, mp 85-90°C, analysis, found: C, 81.80; H, 7.63; N, 6.45; calculated for $C_{29}H_{32}N_2O$:C, 82.04; H, 7.6; N, 6.6. **3b**, colourless needles, mp 169-71°C, analysis found: C, 81.8; H, 7.75; N, 6.48.

Products identification. Identification of the new adducts is mainly based on the 300 MHz NMR spectra (see Table 2). Reported chemical shifts and coupling constants for second-order systems have been corrected. Mass and IR data are in accordance with the reported structure.

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