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THE PHOTOCHEMICAL REACTION BETWEEN 1,4-DICYANONAPHTALENE AND METHYLBENZENES

ELECTRON TRANSFER AND FORMATION OF BENZYLIC RADICALS

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Abstract—The photochemical reaction of 1,4-dicyanonaphtalene (**1**) in the presence of methylbenzenes (**2a–c**) in acetonitrile affords 1 - benzyl - 4 - cyanonaphtalenes (**3**), 1 - benzyl - 1,4 - dicyano - 1,2 - dihydronaphtalenes (**4**), 2 - benzyl - 1,4 - dicyano - 1,2 - dihydronaphtalenes (**5** and **6**) and the tetracyclic derivatives **7** and **8**. Compounds **3**, **7** and **8** are not the products of subsequent transformations of compound **4**. No photochemical reaction is observed in non-polar media, in which, on the contrary, exciplex emission is detected. Experiments in the presence of electron acceptors, electron donors and strong acids support the idea that the reaction is initiated by electron transfer from the methylbenzenes to singlet excited **1**, followed by protolytic equilibrium of the benzylic radical cation to the corresponding radical, which is the attacking species.

While in non-polar medium the excitation of aromatic molecules in the presence of suitable substrates leads to cycloaddition, often through the intermediacy of emitting exciplexes,[1] the change to polar media generally brings about a change both in the photophysics and in the photochemistry of these systems, due to the intervening of full electron transfer from donor D to acceptor A with formation of solvent stabilized radical ions. Although this concept has been known from some time,[2] it is only recently that the synthetic usefulness of photochemistry *via* radical ions has come to be appreciated.[3–6] This kind of photochemistry is indeed multiform, including radical cation (anion) isomerization (eqn 2),[7–10] electrophylic (nucleophylic) reactions of the radical ions (eqn 3),[3,11] reactions between radical ions of opposite sign, either the original ones (eqn 3) or other ones formed by further electron transfer (eqns 5 and 6),†[5,12] cycloaddition,[3,14,15] cationic (anionic) initiated polymerization,[15a] back-electron transfer with formation of other reactive species (eqn 7), e.g. carbonyl oxides from the oxiran radical cation,[9] fragmentation of the radical ions to form radicals (eqn 8).[3]

$$A^* + D \text{ or } D^* + A \rightarrow A^{\cdot -} + D^{\cdot +} \qquad (1)$$

$$D^{\cdot +} \rightarrow B^{\cdot +} \xrightarrow{A^{\cdot -}\quad A} B \qquad (2)$$

$$D^{\cdot +} + C \rightarrow D - C^{\cdot +} \xrightarrow{A^{\cdot -}\quad A} D\text{–}C \qquad (3)$$

$$D^{\cdot +} + A^{\cdot -} \rightarrow D - A \qquad (4)$$

$$A^{\cdot -} + E \rightarrow A + E^{\cdot -} \qquad (5)$$

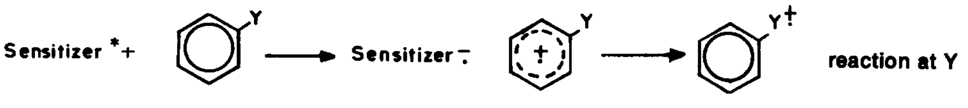
$$D^{\cdot +} + E^{\cdot -} \rightarrow D - E \qquad (6)$$

$$F - G^{\cdot +} \xrightarrow{A^{\cdot -}\quad A} \overset{+}{F} - \overset{-}{G} \qquad (7)$$

$$F - G^{\cdot +}(+L) \rightarrow F^{\cdot} + G^{+} \quad (\text{or } G - L^{+}). \qquad (8)$$

We wish to point out that the process depicted in eqn (8), which is of interest as a mild way to prepare radicals, is little known at present.

A substantial portion of the studies in radical ion photochemistry concern reactions initiated by electron transfer from various phenyl derivatives to the singlet excited state of aromatic molecules bearing electron-withdrawing substituents, such as cyano or carboxyalkyl groups. Phenylalkenes,[3,14,15b] phenylalkynes[14d], phenylcyclopropanes,[7] or cyclopropenes[16] or cyclobutanes,[8] phenyloxirans,[9] β-phenylethyl ethers[3] were found to react in this way. It is assumed that intermolecular electron transfer from the phenyl ring of the donor first takes place, and that the electron is then intramolecularly transfered from the substituted group that eventually reacts (the double bond, the cyclopropane ring, the oxiran ring etc).[7c]



Scheme 1.

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† An example of the latter reaction is offered by the electron transfer photosensitized oxygenations.[10,13]

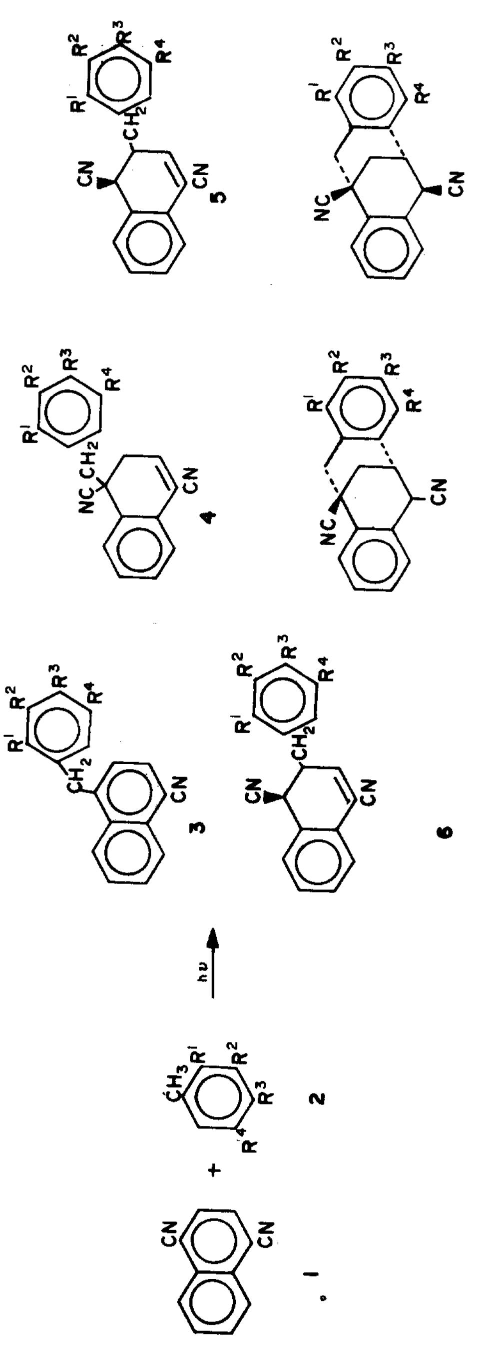
However, no analogue reaction with simple arenes has been reported to date, although many systems can be selected, in which the first step, the intermolecular electron transfer to the excited sensitizer, is spontaneous. The only reported case of this type is the photochemical reaction between 1,2,4,5-tetracyanobenzene and toluene.[17] In this case, however, a preformed ground state complex is irradiated.

Therefore, we chose to examine this problem more closely, and we report here our observations concerning the system 1,4-dicyanonaphthalene (**1**)–methylbenzenes (**2a–c**).‡ In these systems, electron transfer to the singlet excited state of the nitrile is exothermic (*vide infra*) and exciplex emission in non-polar solvents has been reported.[20] Furthermore, no ground state CT complex is evidenced at room temperature, although such a complex is present at low temperature and shows a fluorescence which is identical to the exciplex emission from the non-associated system.[20]

We found that irradiation of these systems in non-polar solvents at room temperature did not cause any reaction, (Experimental) in keeping with the above mentioned finding[17] that the photochemical reaction of tetracyanobenzene in toluene occurs through a pre-existent complex. However, we did observe a reaction on irradiation of the systems **1–2a–c** in acetonitrile, where no exciplex emission was detected—**1** was consumed and new naphthalene derivatives were formed.

In particular, irradiation of **1** in the presence of **2a** (0.3 M) until complete conversion of **1** gave a complex mixture, from which three main products, **3a**, **5a** and **7a** were separated, together with a little **4a** (*vide infra*) and traces of 1,2-diphenylethane. Compound **3a** was shown by its analytical and spectroscopic characteristics to be 1-benzyl-4-cyanonaphthalene. As for product **5a**, its UV spectrum is consistent with a 1,2-dihydro-structure (cf product **10**, *vide infra*), while the interpretation of the ABX system in the PMR spectrum shows the benzyl group to be linked in position 2 and to be in *cis* arrangment with respect to the cyano group in position 1, as the corresponding protons are not in axial–axial configuration ($J_{1,2} = 4.5$ Hz; compare also with the corresponding value for **6c**). As for product **7a**, whose UV spectrum shows the presence of a non-conjugated phenyl group only, its structure of 6,11 - dicyano - 5,11 - methano - 5,6,11,12 - tetrahydrodibenzo[a,c]cyclooctene was determined by single crystal X-ray analysis.

The reaction of **1** with **2b** gave completely analogous results, while in the reaction of **1** with **2c** a more complicate mixture resulted. In both cases, no trace of the



a: $R^1R^2R^3R^4H$ b: R^2R^4Me R^1R^3H c: $R^1R^3R^4Me$ R^2H

Scheme 2.

Table 1. % Product yield from the irradiation of 1 in acetonitrile.

	3	4	5	6	7	8	Notes
2a,0.3M	12	tr[a]	8		23		*b*
2b,0.3M	23		10		26		
2c,0.3M	10	25	24	4	25	5	
2a,0.3M; t-BuCl,0.1M		17	50		13		
2a,0.3M; CF_3COOH,0.01M		6	7		tr		*c*

Notes. *a* tr = traces; *b* 7 mg 1,2-diphenylethane obtained; *c* 45 mg 1,2-diphenylethane obtained; 38% yield product **10**.

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‡Preliminary communication, Ref. 18.

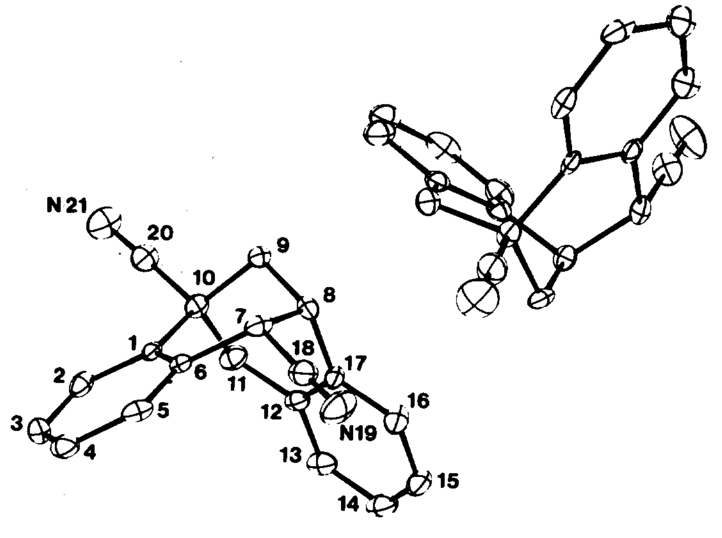
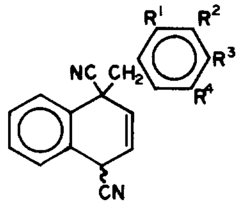


Fig. 1. X-ray structure of compound **7a** showing the two independent molecules in the asymmetric unit.

corresponding diphenylethanes was obtained. Regarding **2c**, compounds **3c**, **5c** and **7c** were still among the main products as in the previous cases. However, minor amounts of **6c** and **8c**, identified from their spectroscopic properties as the geometric isomers of **5c** and **7c** respectively, were obtained. Furthermore a sixth product was obtained in fairly good yield. This product exhibits a UV spectrum consistent again with a 1,2-dihydronaphthalene structure, but, unlike products **5** and **6**, it shows a AB geminal signal in the PMR spectrum, beside the almost superimposed signal due to the magnetically non equivalent benzylic protons. Therefore, this product was identified as 1(2′,4′,5′ - trimethyl)benzyl - 1,4 - dicyano - 1,2 - dihydronaphthalene (**4a**).

A discussion of the mechanism of this reaction should first make it clear whether all products are independently formed. At first sight, the photoproducts can be divided into two groups, the first one including the dihydronaphthalenes **4**, **5** and **6**, which formally arise from the addition of **2** onto **1**, the second one including products **3**, **7** and **8**, which could be envisaged as secondary products arising from dihydronaphthalenes. Indeed, compounds **3** could be the result of the rearomatization through HCN elimination from dihydro derivatives such as **4** or **9**, as has been postulated for the tetracyanobenzene–toluene photoaddition.[17] As for products **7** and **8**, in which a σ bond is formed at the expense of a π bond, they could be the result of a further photoreaction from the same dihydro derivatives **4** and **9**, and also in this case some precedent can be found.[18,21]

In fact products **4a**, c proved to be stable toward rearomatization both under the irradiation conditions and the isolation procedure. Also, while photoreactive both in the presence and in the absence of **1**, products **4** did



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not cyclize to either products **7** or **8**. Furthermore, no compounds of type **9**, which would be the only 1,4-dihydronaphthalenes, were detected among the products of this reaction. Thus, it appears that products **3**, **7** and **8** arise from some other pathway not including a dihydronaphthalene.

This brings us to the question of the mechanism of this photoreaction. The above mentioned difference in the behaviour of the system **1**–**2** in polar or apolar solvents, makes it reasonable to assume that in polar solvents the exciplex (**1**–**2**) collapses to the two solvent stabilized radical ions, an exothermic reaction which has ample precedent.† It remains to be established whether the radical ions of opposite sign then react on re-encounter or some other transformation precedes the formation of the adduct. The first hypothesis seems somewhat unlikely, as such a reaction should conceivably take place also from the exciplex, which is formed in apolar solvents and is equivalent to the excited state of the charge transfer complex (*vide supra*). In this respect, the requirement of a polar medium distinguishes the present reaction from the tetracyanobenzene–toluene photoreaction.[17]

Some clue for the understanding of the present reaction, in our opinion, was found in the following observations (which refer to the reactions of **2a**): (a) The reaction was strongly quenched by oxygen, which would quench **1**$^{\cdot-}$[10,13] as well as radicals which could intervene in the process: (b) The reaction was quenched by low concentration of 1,4-dimethoxybenzene, which would reduce **2**$^{\cdot+}$:[13f] (c) In the presence of 0.01 M trifluoroacetic acid only traces of the normal photoproducts were formed, while reduction to 1,4-dicyano-1,2-dihydronaphthalene (**10**) became the main pathway.

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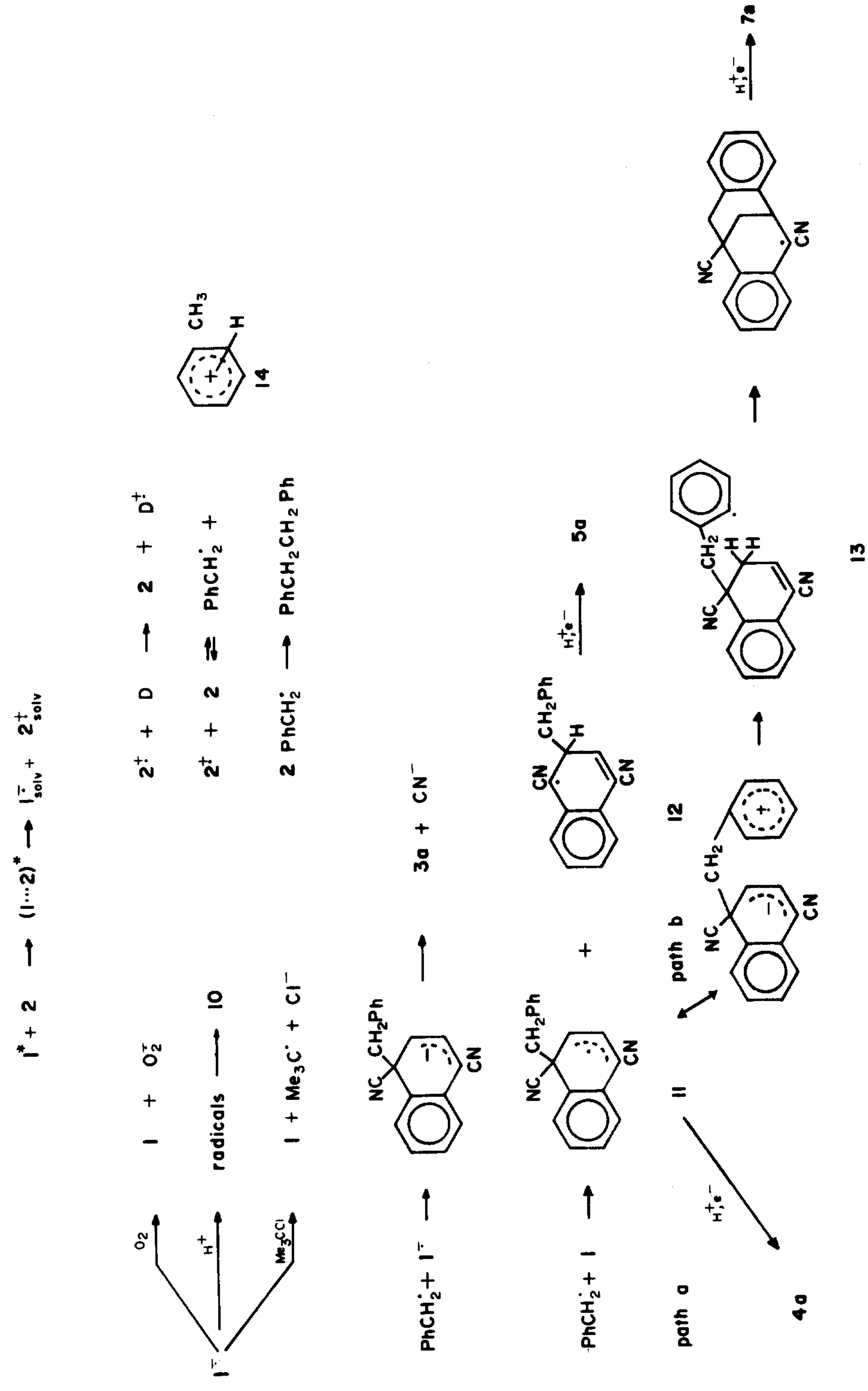
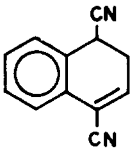
†In the conditions of the experiment the fluorescence of **1** is almost completely quenched by the methylbenzenes. Electron transfer from the singlet excited state is spontaneous (e.g. $\Delta G = -12.5$ kCal/M for durene, taking the oxidation potential from L. Eberson and K. Nyberg, *J. Am. Chem. Soc.* 1966, **88**, 1686), as calculated from the Weller equation.[19] The electron transfer from the triplet state is not spontaneous (e.g. $\Delta G = +18.4$ kCal/M for durene). (compare Ref. 3)


1* + 2 → (1···2)* → 1⁻˙solv + 2⁺˙solv
1⁻˙
O2
H+
Me3CCl
1 + O2⁻˙
radicals → 10
1 + Me3C˙ + Cl⁻
2⁺˙ + D → 2 + D⁺˙
2⁺˙ + 2 ⇌ PhCH2˙ +
2 PhCH2˙ → PhCH2CH2Ph
14
PhCH2˙ + 1⁻˙ →
3a + CN⁻
PhCH2˙ + 1 →
+
12
H+, e⁻
5a
11
path a
path b
H+, e⁻
4a
13
H+, e⁻
7a
NC
CN
CH2Ph
CH2
CH3
H

Scheme 3.



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The formation of **10** is obviously the consequence of the protonation of the radical anion $1^{\cdot-}$. (d) A less dramatic way of affecting the reaction was found in the addition of 0.1M t-butyl chloride. Under these conditions no formation of product **3a** occurred, while products **5a** and **7a** were still formed and product **4a**, which was obtained only in traces in the absence of the halide replaced product **3a**. The alkyl halide would be reduced by $1^{\cdot-}$.[22] On the basis of these observations we propose the following reaction Scheme:

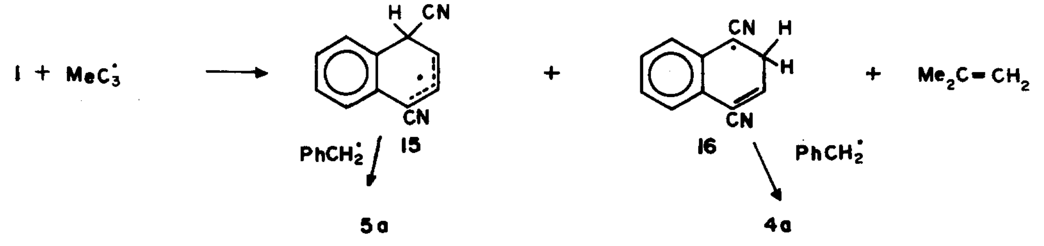
The cation radical $2^{+\cdot}$ transfers a proton to a molecule of toluene forming the corresponding benzylic radical.‡ Benzylic radicals have been shown to display a marked "nucleophylicity" in their reactivity.[24] It is therefore not surprising that these radicals react not only with $1^{\cdot-}$ but also with **1**. The expected coupling of two benzylic radicals to form diphenylethane is only a minor reaction due to the low concentration and to the presence of good traps. This fits with the fact that some diphenylethane was formed in the reaction with toluene, but no substituted diphenylethanes were formed from **2b** or **2c**, the corresponding radicals being still more nucleophylic. The attack of a benzylic radical on $1^{\cdot-}$ leads to a carbanion, from which CN^- elimination leading to **3a** is expected. On the other side the attack of $PhCH_2\cdot$ on **1** leads to radicals **11** and **12**. These give products **4** and **5** by protonation (from **14**) and back electron transfer (from $1^{\cdot-}$). However, a further possibility must be taken into account in the case of radical **11**, i.e. that it directly originates product **7**. A way of visualizing this process is to consider that differently from **12**. Radical **11** has the possibility of taking a convenient conformation with the phenyl ring of the benzylic group nearly parallel to the delocalized radical system and some charge transfer from the former to the latter moiety is to be expected. If such a situation is indeed achieved, proton transfer from the favoured ortho position and radical attack on the acrylic system would bring about radical **13**, the likely precursor of product **7**. If this rationalization holds, it must be expected that while oxygen or 1,4-dimethoxybenzene completely quench the reaction, t-butyl chloride selectively quenches the formation of products **3** by subtracting $1^{\cdot-}$. This is indeed the case and furthermore the formation of product **4** as well as the higher yield of product **5** observed under these conditions can be explained as arising from the reaction of radicals **15** and **16**, in turn formed by further interaction of **1** with the tertiary radical. Note that the radicals **14** and **15** are also the products of the protonation of $1^{\cdot-}$. In fact, product **4** and **5** are formed also in the CF_3COOH experiment.

Some more observation support this view: (a) The reprotonation step to yield products **5** in preference to **6** and **7** in preference to **8** occurs with strong regiospecificity from the less hindered side, in such a way as to allow better interaction with the species which transfers the proton. Only in the case of the derivatives containing the more bulky duryl group is a certain amount of the less favoured diasteroisomeric forms **6c** and respectively **8c** formed. In any case, only the more conjugated 1,2-dihydronaphthalenes are formed, with no trace of 1,4-dihydronaphthalenes. (b) Starting from toluene and mesitylene little or no products **4** are formed, i.e. the intramolecular charge transfer of the radical **11** is so important that path b in Scheme 3 completely overcomes the concurrent path a. However, also in this case the use of durene brings about a change with formation of some **4**, probably owing to the bulkiness of the *o*-Me group, which does not favour the electronically more stable conformation of radical **11**, thus giving more chance to path a. (c) The ratio of the yield of products **7**, **8** and **4** vs the yield of products **5** and **6** is in any case near to 3. This seems a reasonable figure for the relative stability of radical **11** vs radical **12**.

In conclusion, the present data show that benzylic radical cations are formed on interaction between excited naphthalene nitriles and methylbenzenes, and that benzylic radicals deriving from them react with the nitrile to give benzylated products. The necessity of carrying out this reaction in polar medium recalls the abrupt change in going from apolar to polar solvents which has been recently described for the photochemistry of the related aromatic nitriles–alkenes system.[12a] Although more work is needed for the full elucidation of the mechanistic details of the present reaction,† we believe that systems similar to ours could be devised for further synthetic exploitation, particularly as radicals are formed under mild conditions. Some preliminary experiments which are being carried out in our laboratory seem to support this possibility.

EXPERIMENTAL

Materials. 1,4-dicyanonaphthalene was prepared and purified as previously described.[9] Methylbenzenes were purified by dis-



Scheme 4.

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‡Compare the partially analogous situation in Ref. 23.

†An important mechanistic alternative, as recalled also by a Referee, is formation of tigh or solvent separated ion pair within which proton transfer occurs generating proximate radicals which couple (cf the mechanism proposed by Farid in Ref. 14*d*).

Table 2. Melting points and relevant spectroscopic data for photoproducts **3–8** and **10**

	M.P. (°C)	λ max$^{(\log \epsilon)}$	ν_{max}	δ				
				benzylic CH_2				
3a	78–79	231(4.73),289(3.92),299(4.03),311(3.92),324(3.55)	2220	4.4				
3b	88–91	232(4.72),290(3.95),300(4.09),311(3.94),324(3.60)	2210	4.4				
3c	135–36	231(4.81),289(3.92),301(4.03),312(3.92),325(3.57)	2220	4.4				
					ring CH_2	olefinic protons		
4a	oil	222(4.76),276(4.20)	2220,2235	2.95	2.9	6.8		
4c	123–25	221(4.74),271(4.19),280(4.18)	2220,2235	3.0	2.95	6.8		
							$C\begin{smallmatrix}H\\CN\end{smallmatrix}$	
5a	144–45	210(4.49),228(4.23),269(3.93),274(3.95)	2225	3.05		6.6 $J_{2,3} = 3$	3.95 $J_{1,2} = 4.5$	
5b	140–42	221(4.40),228(4.28),273(3.91)	2220	3.0		6.65 $J_{2,3} = 3$	3.95 $J_{1,2} = 5$	
5c	181–83	222(4.47),228(4.39),273(4.00)	2225	3.0		6.7 $J_{2,3} = 3$	4.0 $J_{1,2} = 4$	
6c	178–79	223(4.46),229(4.39),273(4.03)	2235	2.85		6.8 $J_{2,3} = 5$	3.9 $J_{1,2} = 7.5$	
					bridged CH_2			bridgehead CH
7a	231–32	205(4.34),263(2.75),271(2.64)	2235	3.45[a]	2.6		4.5	3.7
7b	178–79	206(4.60),262(2.74),267(2.73)	2235	3.4[a]	2.55		4.5	3.7
7c	182–83	204(5.04),262(3.02),270(3.08),275(3.05),280(2.99)	2235	3.0	2.75		4.4	4.0
8c	188–90	204(4.69),256(2.89),263(2.96),270(2.99),280(2.89)	2240	3.3	2.45		4.55	3.9
					ring CH_2			
10	92	207(4.16),222(4.18),270(3.87),	2220,2240		2.8	6.85t J = 5	4.1	

[a] Center of the AB system; l gem = 8 Hz.

tillation or crystallization. Spectrograde acetonitrile was used as received.

Photochemical reactions. 70 ml of an acetonitrile soln containing 250 mg (1.4 mM) of **1** and 21 mM of the appropriate methylbenzene were flushed with purified N_2 and irradiated with a Pyrex-filtered 150 W medium pressure mercury lamp at 17° until **1** was almost completely converted (tlc). After evaporation of the solvent, the photolysate was chromatographed on silica gel eluting with cyclohexane in order to eliminate the residual methylbenzenes and then with cyclohexane–EtOAc mixtures. In some cases repeated chromatography was needed in order to achieve a satisfactory separation. The photoproducts were then purified by crystallization from cyclohexane (products **3**), benzene–cyclohexane (products **4**, **5**, **6**, **8** and **10**), toluene (products **7**). In the trifluoroacetic acid experiment the raw photolysate was dissolved in benzene and shaken with NaOH aq before chromatography. The tests on the conversion of product **4c** were carried out by submitting a pure sample to the same isolation procedure as before. The product was recovered unchanged. Furthermore, compound **4c** was irradiated in acetonitrile soln both with a low pressure mercury arc through quartz and with a medium pressure mercury arc through Pyrex in the presence of **1**. In both cases reaction was observed, but neither products **7c** nor **8c** were detected by tlc.

Table 3. Elemental analysis for photoproducts **3–8** and **10**

	Found			Required		
	C	H	N	C	H	N
3a	88.94	5.38	5.88	88.86	5.39	5.76
5a	84.42	5.50	10.40	84.42	5.22	10.36
7a	84.69	5.22	10.42			
3b	88.93	6.38	5.15	88.59	6.32	5.16
5b	84.89	6.18	9.37	84.53	6.08	9.39
7b	84.33	6.10	9.40			
3c	88.50	6.79	4.88	88.30	6.79	4.88
4c	84.24	6.47	9.08	84.58	6.45	8.97
5c	85.00	6.59	9.18			
6c	84.85	6.56	9.20			
7c	84.90	6.83	8.81			
8c	84.33	6.49	9.20			
10	80.14	4.70	15.68	79.98	4.48	15.55

Irradiation of **1** in the presence of methylbenzenes in cyclohexane yielded no appreciable amount of new products after several days irradiation. In these conditions the already reported[20] exciplex emission was observed.

Characterisation of the photoproducts. UV spectra were recorded in EtOH with a Perkin–Elmer 200 spectrophotometer. IR spectra were recorded in nujol mull or in KBr pellets by means of a Perkin–Elmer 197 spectrophotometer. PMR spectra were recorded in CCl_4 (products **3**) or $CDCl_3$ (the other products) by means of a Perkin–Elmer R12 instrument with TMS as internal standard. The relevant data are reported in Table 2. All compounds gave correct analytical data (Table 3).

Structure of product **7a**. The conditions of the X-ray structure determination for this compound have been reported in a preliminary note.[18] It must be observed that the elementary cell is occupied by two enentiomeric molecules, which significantly differ in their conformation. The molecules are folded (see the

Table 4. Equations of least-squares planes for the two benzene rings in product **7a**

C1–C6 (mean deviation = 0.0006 A):
$8.7147x - 9.8606\ y - 6.41927\ z - 1.3171 = 0$
C12–C17 (mean deviation = 0.0009 A):
$13.2432\ x + 2.9674\ y + 5.4069\ z - 14.1396 = 0$
Interplanar angle = 89.7°.
C1′–C6′ (mean deviation = 0.0005 A)
$13.3243\ x + 5.9009\ y - 4.7575\ z - 8.4234 = 0$
C12′–C17′ mean deviation = 0.0004 A):
$8.5559\ x - 10.9555\ y + 5.6460\ z - 8.3732 = 0$
Interplanar angle = −88.0°.

Table 5. Relevant torsion angles (°). Standard deviations in parentheses for product **7a**

C10 - C 1 - C 2 - C 3	3.1 (4)	C10' - C 1' - C 2' - C 3'	-3.6 (3)
C 2 - C 1 - C 6 - C 7	0.3 (4)	C 2' - C 1' - C 6' - C 7'	1.5 (3)
C10 - C 1 - C 6 - C 5	-1.7 (3)	C10' - C 1' - C 6' - C 5'	2.7 (4)
C10 - C 1 - C 6 - C 7	177.8 (4)	C10' - C 1' - C 6' - C 7'	-175.8 (3)
C 2 - C 1 - C10 - C 9	15.8 (4)	C 2' - C 1' - C10' - C 9'	-15.7 (3)
C 2 - C 1 - C10 - C11	-104.2 (4)	C 2' - C 1' - C10' - C11'	105.3 (4)
C 2 - C 1 - C10 - C20	137.6 (4)	C 2' - C 1' - C10' - C20'	-13 .0 (4)
C 6 - C 1 - C10 - C 9	-161.6 (5)	C 6' - C 1' - C10' - C 9'	161.6 (4)
C 6 - C 1 - C10 - C11	78.4 (3)	C 6' - C 1' - C10' - C11'	-77.4 (3)
C 6 - C 1 - C10 - C20	-39.8 (3)	C 6' - C 1' - C10' - C20'	41.3 (4)
C 4 - C 5 - C 6 - C 7	-0.7 (4)	C 4' - C 5' - C 6' - C 7'	-0.1 (3)
C 1 - C 6 - C 7 - C 8	-159.4 (4)	C 1' - C 6' - C 7' - C 8'	155.5 (4)
C 5 - C 6 - C 7 - C 8	20.1 (3)	C 5' - C 6' - C 7' - C 8'	-23.0 (3)
C 5 - C 6 - C 7 - C18	145.9 (4)	C 5' - C 6' - C 7' - C18'	-150.7 (4)
C 6 - C 7 - C 8 - C 9	126.2 (3)	C 6' - C 7' - C 8' - C 9'	-122.7 (4)
C 6 - C 7 - C 8 - C17	-110.9 (3)	C 6' - C 7' - C 8' - C17'	114.9 (4)
C18 - C 7 - C 8 - C17	124.2 (4)	C18' - C 7' - C 8' - C17'	-117.2 (4)
C 6 - C 7 - C18 - N19	-106.9(10)	C 6' - C 7' - C18' - N19'	41.5 (5)
C 8 - C 7 - C18 - N19	19.5 (1)	C 8' - C 7' - C18' - N19'	-85.7 (5)
C 7 - C 8 - C 9 - C10	-109.3 (3)	C 7' - C 8' - C 9' - C10'	108.8 (3)
C17 - C 8 - C 9 - C10	127.0 (3)	C17' - C 8' - C 9' - C10'	-126.4 (3)
C 7 - C 8 - C17 - C12	81.9 (3)	C 7' - C 8' - C17' - C12'	-81.1 (5)
C 7 - C 8 - C17 - C16	-97.3 (4)	C 7' - C 8' - C17' - C16'	100.4 (4)
C 9 - C 8 - C17 - C12	-158.6 (4)	C 9' - C 8' - C17' - C12'	158.9 (5)
C 9 - C 8 - C17 - C16	22.2 (4)	C 9' - C 8' - C17' - C16'	-19.6 (3)
C 8 - C 9 - C10 - C 1	127.2 (4)	C 8' - C 9' - C10' - C 1'	-129.0 (3)
C 8 - C 9 - C10 - C11	-111.5 (3)	C 8' - C 9' - C10' - C11'	108.4 (4)
C 8 - C 9 - C10 - C20	6.7 (4)	C 8' - C 9' - C10' - C20'	-8.0 (3)
C 1 - C10 - C11 - C12	-108.2 (4)	C 1' - C10' - C11' - C12'	109.5 (3)
C 9 - C10 - C11 - C12	129.9 (4)	C 9' - C10' - C11' - C12'	-126.6 (3)
C20 - C10 - C11 - C12	10.1 (4)	C20' - C10' - C11' - C12'	-10.1 (3)
C 1 - C10 - C20 - N21	8.6 (3)	C 1' - C10' - C20' - N21'	101.9 (4)
C 9 - C10 - C20 - N21	131.9 (4)	C 9' - C10' - C20' - N21'	-21.3 (4)
C10 - C11 - C12 - C13	17.1 (4)	C10' - C11' - C12' - C13'	-17.4 (3)
C10 - C11 - C12- C17	-161.0 (4)	C10' - C11' - C12' - C17'	160.2 (4)
C11 - C12 - C13 - C14	2.8 (5)	C11' - C12' - C13' - C14'	-1.2 (3)
C11 - C12 - C17 - C 8	175.9 (4)	C11' - C12' - C17' - C 8'	-176.3 (6)
C11 - C12 - C17 - C16	-4.9 (4)	C11' - C12' - C17' - C16'	2.2 (3)
C13 - C12 - C17 - C 8	-2.3 (3)	C13' - C12' - C17' - C 8'	1.2 (5)
C15 - C16 - C17 - C 8	2.5 (3)	C15' - C16' - C17' - C 8'	-2.1 (4)
C15 - C16 - C17 - C12	-176.7 (5)	C15' - C16' - C17' - C12'	179.3 (5)

dihedral angle between the planes of the two benzene rings, which is different in the two conformations). The position of the cyano groups also significantly differs.

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