

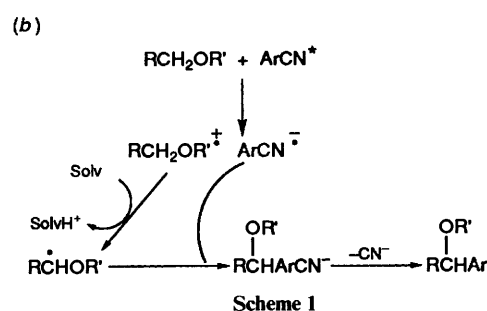
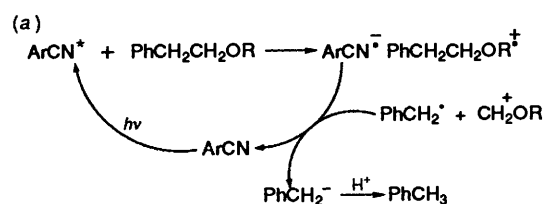
## Aliphatic Radicals from Ethers *via* Photoinduced Electron Transfer: Selective Formation and Chemistry

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Irradiation of aliphatic ethers in the presence of benzene-1,2,4,5-tetracyanobenzene (TCB) has been found to cause electron transfer. The radical cations of methyl *tert*-butyl ether and of 1,4-dioxane are deprotonated under these conditions, and in the case of methyl neopentyl ether, both C–C and C–H bond cleavage take place. The selectivity of the cleavage is rationalized on the basis of thermochemical considerations. The alkyl radicals thus formed add to the TCB radical anion (thus aromatic substitution results) or are trapped with acrylonitrile, followed by coupling with TCB<sup>•-</sup> (radical–alkene addition, followed by aromatic substitution).

Ethers are moderate electron donors and previous work has shown that they can be oxidized through photoinduced single electron transfer (PET) by excited acceptors such as aromatic nitriles. Two different reactions have been reported. The first one is 'mesolytic' cleavage of 2-phenylethyl ethers to yield toluene, which involves C–C bond cleavage from the ether radical cation and reduction of the benzyl radical by the acceptor radical anion [Scheme 1(a)].<sup>1,2</sup> The second reaction is



an aromatic substitution involving  $\alpha$ -deprotonation of the ether radical cation, combination of the neutral radical with the acceptor radical anion and cyanide loss from the resulting anion [Scheme 1(b)]. This has been reported for aliphatic ethers with 1,2,4,5-tetracyanobenzene (TCB)<sup>3</sup> (a related reaction occurs with tetrahalophthalimides)<sup>4</sup> and 9,10-dicyanoanthracene<sup>5</sup> as well as for benzyl ethers with 1,4-dicyanonaphthalene (DCN).<sup>6</sup>

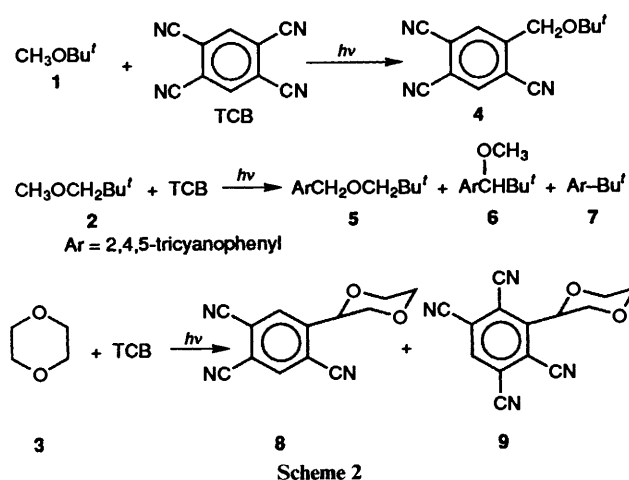
Our continuing interest in PET chemistry<sup>7,8</sup> led us to examine further this class of donors with a twofold objective, *viz* (a) to study the competition between mesolytic cleavage and  $\alpha$ -deprotonation and (b) to explore whether trapping of the radicals formed in these processes through addition reactions may lead to reactions of synthetic significance.

The substrates chosen were methyl *tert*-butyl ether (1) ( $\alpha$ -deprotonation expected), methyl neopentyl ether (2) (two competitive  $\alpha$ -deprotonations and mesolytic C–C cleavage are possible) and 1,4-dioxane (3) ( $\alpha$ -deprotonation and C–C bond cleavage are possible, the latter one giving a distonic radical cation). The high oxidation potential of these substrates

requires that a strong photochemical oxidant is used and we chose TCB.

### Results

**Preparative Irradiation.**—Irradiation (320 nm) of ether 1 (0.1 mol dm<sup>-3</sup>) and TCB (5 × 10<sup>-3</sup> mol dm<sup>-3</sup>) in deaerated acetonitrile, followed by chromatographic separation gave a single compound, identified as the alkylated trinitrile 4 from its analytical and spectroscopic properties (Scheme 2, Table 1, see



Experimental for characterization). In the case of ether 2 three alkylated trinitriles were obtained and were recognized as the two ethers 5 and 6 and the *tert*-butyl derivative 7. Dioxane 3 gave the alkyltricyanobenzene 8 as the main product, accompanied by a minor amount of the alkyl tetracyanobenzene 9.

**Irradiation in the Presence of Acrylonitrile.**—Separate irradiations were carried out under the same conditions in the

**Table 1** Products from the irradiation of TCB and ethers 1–3 in acetonitrile

Ether	Product [Yield (%)]	
	in MeCN	in MeCN with 5 × 10 <sup>-2</sup> mol dm <sup>-3</sup> AN
1	4 (35)	4 (35), 10 (25)
2	5 (21), 6 (20), 7 (15)	5 + 6 + 7 (tr), 11 (11), 12 (47), 13 (10)
3	8 (20), 9 (5)	

**Table 2** Photophysical parameters for the reaction of TCB with ethers 1–3

Ether	$E_{ox}/V$ vs. SCE	$\Delta_{cl}G^a/eV$	$K_{SV}/mol^{-1}$	$k_q/10^9 dm^3 mol^{-1} s^{-1}$	$\Phi_r^b$
1	2.73	-0.7	58	5.4	0.065
2	2.73	-0.7	60	5.5	0.06
3	1.97	-1.4	149	13	0.012

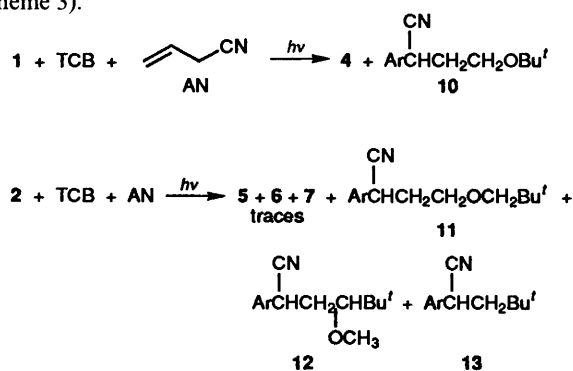
<sup>a</sup> Free energy change for electron transfer to singlet excited TCB calculated according to the Weller equation. <sup>b</sup> At 0.1 mol dm<sup>-3</sup> ether concentration.

**Table 3** Calculated enthalpy change for radical cation fragmentation<sup>a</sup>

Reaction	$\Delta H$	$\Delta_{cl}H$
Me <sub>2</sub> O <sup>+</sup> → MeOCH <sub>2</sub> <sup>+</sup> + H <sup>+</sup>	93	-21
1,4-Dioxane <sup>+</sup> → 1,4-dioxan-2-yl + H <sup>+</sup>	92	-1
Bu <sup>t</sup> CH <sub>2</sub> OMe <sup>+</sup> → Bu <sup>t</sup> + MeOCH <sub>2</sub> <sup>+</sup>	69.5	+1
PhCH <sub>2</sub> CH <sub>2</sub> OMe <sup>+</sup> → PhCH <sub>2</sub> <sup>+</sup> + MeOCH <sub>2</sub> <sup>+</sup>	69	+10

<sup>a</sup> According to eqn. (4); values used:  $E_i(\text{Me}_2\text{O})$ , 10.04 eV;<sup>9</sup>  $E_i(\mathbf{2})$  is assumed to be the same as for MeOEt, 9.86 eV;<sup>9</sup>  $E_i$  values are converted to  $E_{ox}$  by means of the Miller equation;<sup>10</sup>  $E_{ox}(\mathbf{3})$ , 1.97 V;<sup>10</sup>  $E_{ox}(\text{PhCH}_2\text{CH}_2\text{OMe})$ , 2.29 V;  $E_{ox}(\text{MeOCH}_2^+)$  -0.24 V;<sup>12</sup>  $E_d(\text{PhCH}_2\text{-CH}_2\text{OMe})$  is assumed to be the same as for PhCH<sub>2</sub>-Et.<sup>19</sup>

presence of  $5 \times 10^{-2}$  mol dm<sup>-3</sup> acrylonitrile (AN), with the aim of demonstrating the intermediacy of radicals and their mode of reaction. Thus, from TCB, **1** and AN two compounds were obtained, the previously mentioned ether **4** and a product incorporating AN, which was shown to have structure **10** (Scheme 3).



Scheme 3

From the irradiation of TCB, **2**, and AN, the three trinitriles **5–7** were obtained only in traces, while three new compounds incorporating AN were formed in overall good yield. These were shown to have structures **11–13**.

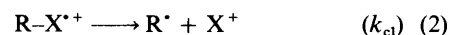
**Mechanistic Observations.**—In order to determine the mechanism of these reactions some measurements were carried out as follows. Thus, at the concentrations considered, the UV spectra of the TCB–ether solutions in MeCN correspond to the sum of the spectra of the solutions of each reagent alone. All the ethers efficiently quenched the fluorescence of TCB, with **3** reaching the diffusion controlled limit. The quantum yield of the reaction of TCB was measured with a 0.1 mol dm<sup>-3</sup> ether concentration (in view of the high  $K_{SV}$  values, these were close to the  $\Phi_{lim}$  value). The data are gathered in Table 2.

## Discussion

The mechanism of the present reaction follows the same pattern of previously reported PET-induced radical aromatic substitutions [Scheme 1(b), the formation of product **9** is a partial exception, see below], with the peculiarity that the radical

cations undergo competitively both deprotonation and C–C bond cleavage, and both types of radicals participate in the alkylation reaction.

**Efficiency and Selectivity in the Radical Cation Cleavage.**—The reaction is initiated by electron transfer from the ether to singlet-excited TCB, as indicated by the fact that fluorescence quenching is efficient and grows with decreasing ether oxidation potential, as well as by the negative  $\Delta_{cl}G$ , as calculated with the Weller equation (Table 2). The radical cation then fragments, and this is again a rather efficient process, as indicated by the relatively high  $\Phi_{lim} = k_{cl}/(k_{cl} + k_{bet})$  values. This requires that the rate constant for cleavage  $k_{cl}$  is greater than  $10^8$  s<sup>-1</sup>.



The enthalpy change for the cleavage of a radical cation  $\text{R-X}^{\cdot+}$  [ $\Delta_{cl}H$ ] [eqn. (2)] can be evaluated by means of eqns. (4) or (5),<sup>7</sup> which show that the bond weakening caused by oxidation [ $\Delta\Delta_{cl}H$ ] is equal to the difference between the oxidation potential of the starting substrate and that of the radical corresponding to the electrofugal group X<sup>+</sup>. Since radicals are oxidized (and reduced) more easily than the corresponding neutral molecules, a conspicuous lowering of the bond strength takes place upon electron transfer.

$$\Delta_{cl}H = \Delta H + F[E^{\text{ox}}_{\frac{1}{2}}(\text{X}^{\cdot+}) - E^{\text{ox}}_{\frac{1}{2}}(\text{R-X})] \quad (4)$$

$$\Delta\Delta_{cl}H = \Delta H - \Delta_{cl}H = F[E^{\text{ox}}_{\frac{1}{2}}(\text{R-X}) - E^{\text{ox}}_{\frac{1}{2}}(\text{X}^{\cdot+})] \quad (5)$$

Some data relevant to the present case are reported in Table 3, e.g. deprotonation of the radical cation of dimethyl ether is a strongly exothermic process (from the thermodynamic point of view, this is a very strong acid). In proceeding along the series **1–3** the oxidation potential of the substrate drops more than the C–H bond energy [ $E^{\text{ox}}_{\frac{1}{2}}$  for Me<sub>2</sub>O is 2.89 V vs. SCE, as evaluated from the PES value<sup>9</sup> through the Miller equation,<sup>10</sup> while  $E^{\text{ox}}_{\frac{1}{2}}$  for **3** is 1.97 V (measured in solution)<sup>10</sup>]. However, the  $\Delta_{cl}H$  for deprotonation remains negative, although less strongly so, also for **3**.

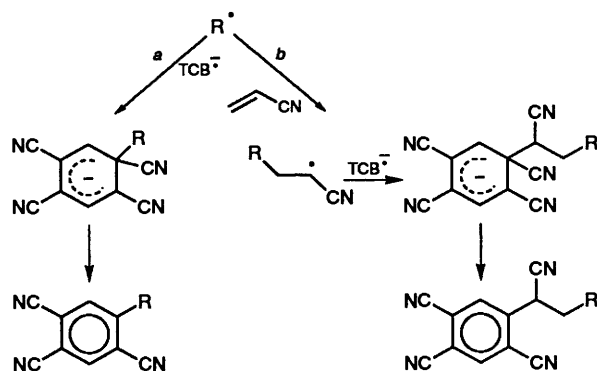
The thermodynamics of C–C bond cleavage is less precisely evaluated, because the required energy data have not been reported and so we used  $E_d$  values for related compounds. The fragmentation is thermoneutral for the neopentyl ether **2** and somewhat endothermic for phenyl ethyl ether. Previous experience<sup>7</sup> with other donors consistently showed that, provided it is at most endothermic by a few kcal mol<sup>-1</sup>, C–C fragmentation is more efficient than deprotonation: the latter reaction is always more exothermic, but is kinetically unfavourable unless the radical anion is a good nucleophile (which is not the case here: it has been demonstrated that the radical anions of aromatic nitriles are very poor bases).<sup>11a</sup> The present results with **2** fully comply with this generalization. In the case of **3**, the drop of 0.85 V in  $E_{ox}$  with respect to ether **2**

largely compensates for the weakening of the C–C bond and  $\Delta_{\text{cl}}H$  is  $>10$  kcal mol $^{-1}$ , making this process too slow to compete.<sup>†</sup> This explains why only deprotonation is observed with  $3^{*+}$ .

Note also that with the better donor **3** quenching of TCB\* is more efficient than with either **1** or **2**, but the efficiency of the photoreaction is lower. This may be due to an increased rate of back electron transfer, which is expected in this case since the reaction occurs in the inverted Marcus region.<sup>11b</sup>

**Reactions of the Radicals.**—**Reaction with the radical anion.** Another difference between Schemes 1(a) and (b) is that the radicals are reduced by the acceptor radical anion in the first case, while coupling between the two electron-unpaired species results in the latter one. This depends on the relevant redox potentials. Ground state TCB is easily reduced ( $E_{\text{red}} -0.7$  V vs. SCE) and thus electron transfer from its radical anion to alkyl radicals is too endothermic [e.g.  $E_{\text{red}}(\text{Bu}^{\bullet}) < -2$ ,  $E_{\text{red}}(\text{MeOCH}_2^{\bullet}) -1.3$  V].<sup>12</sup> Indeed, examination of the previous literature<sup>2,13,14</sup> shows that reductive cleavage of benzyl derivatives according to Scheme 1(a) requires that the reduction potential of the acceptor is more negative than that of the benzyl radical ( $E_{\text{red}} -1.45$  V),<sup>12</sup> a condition met e.g. with 1,4-dicyanobenzene ( $E_{\text{red}} -1.62$  V), but not with 1,4-dicyanophthalene (DCN,  $E_{\text{red}} -1.28$  V); indeed, when the latter acceptor is used the ether is cleaved, but DCN is concurrently decomposed to an uncharacterized mixture of products.<sup>15</sup>

In cases when radical coupling takes place, it invariably occurs at the position of the radical anion with the highest spin density<sup>16,17</sup> (the substituted position in TCB $^{\bullet-}$ , see Scheme 4,

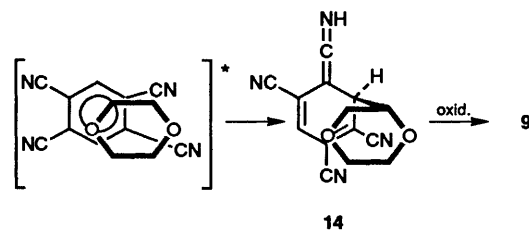


Scheme 4

path a). The tricyanobenzenes **4–8** follow the expected path, similar to that observed when the radical arises from different precursors. However, with dioxane some alkylation at the unsubstituted position (to yield **9**) occurs, at least as a minor path, since the main product is the expected **8**. A different mechanism appears to be operating in this case. One possibility would be a reaction *via* a tight exciplex (favoured by the particular structure of the donor, with the two  $n_{\text{O}}$  donating orbitals sitting opposite to the negative charge in the polarized acceptor, see Scheme 5) leading to proton exchange within the pair and C–C bond formation to yield the intermediate **14**, which would then undergo oxidation through a path (which at the moment is unspecified). At any rate, whatever the mechanism for the formation of **9** might be, this does not change the conclusions about the selectivity in the radical cation cleavage discussed above.

**Addition to alkenes.** The  $\alpha$ -alkoxyalkyl and alkyl radicals

<sup>†</sup> A Referee suggests that the lack of C–C cleavage in  $3^{*+}$  is due to stereoelectronic factors. Indeed, in this case the ring C–C bond cannot become aligned with the half vacant  $n_{\text{O}}$  orbital.



Scheme 5

formed according to eqn. (2) are nucleophilic species. Indeed, in the presence of an electron-withdrawing substituted alkene, e.g. acrylonitrile, addition reactions compete with the alkylation of TCB and the AN addition compounds **10–13** are obtained together with (in the case of **1**) or in the place of (in the case of **2**) the products of aromatic substitution. This is rationalized on the basis of accepted tenets of radical chemistry. Thus, the alkyl radical is trapped by AN to yield a radical adduct (Scheme 4, path b). The latter is a stabilized species, and coupling with the TCB radical anion predominates over any competing reaction, giving products **10–13** in good chemical yield (the acronym ROCAS, Radical Olefin Coupling Aromatic Substitution can be used to designate the overall process), with no attending AN polymerization. In the case of ether **2**, where different radicals are formed, the ratio between the products arising from each radical is different in direct aromatic substitution (compounds **5–7**) and in the ROCAS process (compounds **11–13**), indicating that the mechanism is probably not as simple as proposed. However, the fact that this ordered three component addition is obtained in a fair yield points to a possible synthetic significance of the method, which should be ascertained through a study devoted to this end.

## Conclusion

The radical cations of aliphatic ethers are generated by PET with TCB. The cleavage of these species competes efficiently with back electron transfer and this can be considered a suitable method for obtaining free radicals under exceptionally mild conditions. The radicals couple with the TCB radical anion giving alkylated trinitriles, but they can also be trapped by acrylonitrile to yield products of aromatic substitution incorporating AN. This suggests that the scope of this PET cleavage may be considerably enlarged to give synthetically useful reactions.

## Experimental

The ether **2** was prepared by phase-transfer alkylation of the alcohol.<sup>18</sup> The other reagents and solvents were of commercial origin.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AC 300 MHz spectrometer in  $\text{CDCl}_3$  solutions and chemical shifts are reported in ppm downfield from  $\text{Me}_4\text{Si}$

**Preparative Irradiation.**—100 cm $^3$  of a  $5 \times 10^{-3}$  mol dm $^{-3}$  solution of TCB and 0.1 mol dm $^{-3}$  of the ether **1** in acetonitrile was equally divided in five septum-capped quartz tubes and purged with argon. The tubes were irradiated for 1 h in a multilamp apparatus fitted with six 15 W phosphor-coated lamps, with a centre of emission at 320 nm. Evaporation of the solvent and chromatography of the residue on silica gel (eluting with cyclohexane–ethyl acetate, 9:1 mixture) gave 5-(*tert*-butoxymethyl)benzene-1,2,4-tricarbonitrile (**4**) (44.5 mg, 35% yield). Mp 97–99 °C (MeOH) (Found: C, 70.6; H, 5.7; N, 17.2. Calc. for  $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}$ : C, 70.27; H, 5.48; N, 17.56%);  $\delta_{\text{H}}$ (300 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 1.32 (9 H, s), 4.70 (2 H, s), 8.02 (1 H, s) and 8.18 (1 H, s).

The other preparative reactions were similarly carried out, as detailed in Table 1, in the presence of  $5 \times 10^{-2}$  mol dm<sup>-3</sup> acrylonitrile when appropriate. The following products were obtained (compound **7** and **13** had been previously reported).<sup>19</sup>

**5-(Neopentylloxymethyl)benzene-1,2,4-tricarbonitrile (5)**.—Mp 153–155 °C (MeOH) (Found: C, 71.0; H, 5.6; N, 16.3. Calc. for C<sub>15</sub>H<sub>15</sub>N<sub>3</sub>O: C, 71.12; H, 5.97; N, 16.59%);  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 1.02 (9 H, s), 3.32 (2 H, s), 4.78 (2 H, s), 8.07 (1 H, s) and 8.12 (1 H, s).

**5-(1-Methoxy-2,2-dimethylpropyl)benzene-1,2,4-tricarbonitrile (6)**.—Mp 105–107 °C (MeOH) (Found: C, 70.9; H, 5.9; N, 16.3%)  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 0.95 (9 H, s), 3.25 (3 H, s), 4.3 (1 H, s), 8.0 (1 H, s) and 8.05 (1 H, s).

**2-(2,4,5-Tricyanophenyl)-1,4-dioxane (8)**.—Mp 128–130 °C (MeOH) (Found: C, 64.9; H, 3.8; N, 17.5. Calc. for C<sub>13</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub>: C, 65.26; H, 3.79; N, 17.57%)  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 3.3 (1 H, dd, *J* 10, 11 Hz, 3-H), 3.7–4.5 (4 H, m, 5-H, 6-H), 4.08 (1 H, dd, *J* 2.5, 10, 3-H), 5.05 (1 H, dd, *J* 3, 10 Hz, 2-H) and 8.05 (1 H, s) and 8.2 (1 H, s);  $\delta_{\text{C}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 66.0 (CH<sub>2</sub>), 66.8 (CH<sub>2</sub>), 70.5 (CH<sub>2</sub>), 74.6 (CH), 113.3, 113.5, 113.8 (CN), 115.1 (CN), 116.0, 119.8 (CN), 132.6 (CH), 136.6 (CH) and 147.6.

**2-(2,3,5,6-Tetracyanophenyl)-1,4-dioxane (9)**.—The sample obtained was mixed with **8**, and the small quantity made purification difficult. *m/z* 269 (M<sup>+</sup>);  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 3.7–4.1 (6 H, m, 3-, 5-, 6-H), 5.3 (dd, *J* 3, 10 Hz, 2-H) and 8.15 (1 H, s);  $\delta_{\text{C}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 65.6, 66.6, 68.4, 75.0 (CH), 111.6, 112.5, 119.6 (CN), 121.7 (CN), 136.1 (CH) and 147.8.

**5-(3-tert-Butoxy-1-cyanopropyl)benzene-1,2,4-tricarbonitrile (10)**.—Mp 140–142 °C (MeOH) (Found: C, 69.9; H, 5.5; N, 19.3. Calc. for C<sub>17</sub>H<sub>16</sub>N<sub>4</sub>O: C, 69.84; H, 5.52; N, 19.17%)  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 1.18 (9 H, s), 2.25 (2 H, m), 3.6 (2 H, m), 4.62 (1 H, dd, *J* 6, 7 Hz), 8.08 (1 H, s) and 8.15 (1 H, s).

**5-(1-Cyano-3-neopentylpropyl)benzene-1,2,4-tricarbonitrile (11)**.—Mp 125–127 °C (MeOH) (Found: C, 70.5; H, 5.8; N, 18.2. Calc. for C<sub>18</sub>H<sub>18</sub>N<sub>4</sub>O: C, 70.56; H, 5.92; N, 18.29%)  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 0.9 (9 H, s), 2.25 (2 H, m, 2'-H), 3.1 (AB system, 2 H, Bu<sup>+</sup>CH<sub>2</sub>O), 3.7 (2 H, m, 3'-H), 4.65 (1 H, dd, *J* 5, 8 Hz, 1'-H), 8.05 (1 H, s) and 8.08 (1 H, s).

**5-(1-Cyano-4,4-dimethyl-3-methoxypropyl)benzene-1,2,4-tricarbonitrile (12)**.—Mp 130–132 °C (MeOH) (Found: C, 70.7; H, 5.8; N, 18.2%). Two diastereoisomers: the first one,  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 0.97 (9 H, s), 1.88 (1 H, ddd, *J* 4.5, 11, 15 Hz) and 2.1 (1 H, ddd, *J* 2, 11.5, 15, 2'-H), 3.15 (1 H, dd, *J* 2, 11 Hz, 3'-H), 4.6 (1 H, dd, *J* 4.5, 11.5 Hz, 1'-H) and 8.15 (1 H, s), 8.17 (1 H, s); the other one,  $\delta_{\text{H}}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 0.95 (9 H, s), 2.15 (2 H, m, 2'-H), 2.95 (1 H, dd, *J* 5, 7 Hz, 3'-H), 4.35 (1 H, t, *J* 7 Hz, 2-H) and 8.15 (1 H, s) and 8.2 (1 H, s).

**Quantum Yield Measurements**.—Quantum yields were measured on similarly prepared deaerated solution as aliquots (5 cm<sup>3</sup>) in septum-capped quartz tubes. These were irradiated as above in a rotating merry-go-round; substrate conversion was <25%; product formation was determined by VPC with dodecane as an internal standard.

**Fluorescence Quenching**.—Fluorescence intensities were measured by means of an Aminco-Bowman MPF spectro-photometer on deaerated solutions in 1 cm optical cuvettes.

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