# Benzyl Radicals from Toluene by Photosensitization with Naphthalene-1,4-dicarbonitrile – Benzylation and Hydroxymethylation of Unsaturated Compounds

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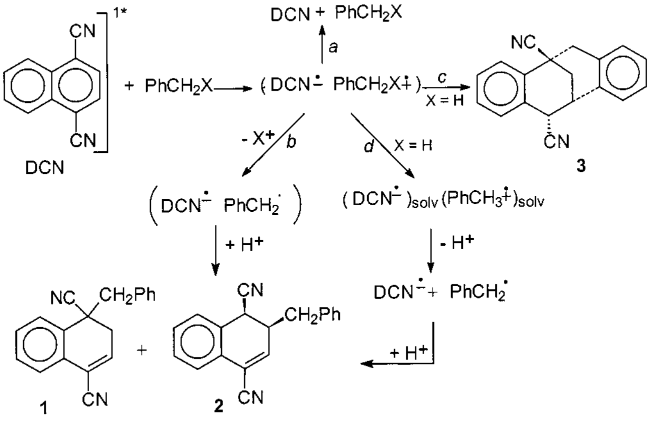
In aprotic media, photoinduced electron transfer from toluene to 1,4-naphthalenedicarbonitrile (DCN) is followed by in-cage proton transfer and radical coupling. However, in the presence of a protic co-solvent, the radical ions diffuse out of the cage and deprotonation of the toluene radical cation takes place from the free solvated species. With *t*BuOH, this results in reductive benzylation of DCN through coupling of benzyl radicals with $DCN^{-\cdot}$. With MeOH, secondary hydrogen abstraction by $PhCH_2\cdot$ yields hydroxymethyl radicals, which couple with $DCN^{-\cdot}$. Both benzyl and hydroxymethyl radicals are efficiently trapped by electrophilic alkenes. Thus, in the presence of dimethyl maleate, DCN-photosensitized benzylation – or hydroxymethylation – of the substrate occurs through direct activation of the C–H bond. The same reaction has been accomplished with acrylonitrile, albeit with a lower yield.

## Introduction

Aromatic nitriles are strong oxidants in the singlet excited state.[1] Quenching by a variety of donors, which can be conveniently monitored through fluorescence quenching, leads to a radical ion pair. The chemical outcome not only depends on the radical ions, but also on the solvent or medium. If no chemical process is sufficiently fast, back electron transfer ensues and the overall process is limited to physical quenching. Many radical ions, however, undergo a fast fragmentation, and then a photosensitized reaction occurs with a reasonable quantum yield (>0.1).[2]

A typical example is that of 1,4-naphthalenedicarbonitrile (DCN) in the presence of benzylic donors, the photochemistry of which in polar, aprotic solvents such as acetonitrile has been extensively studied.[3] After initial electron transfer (see Scheme 1), the chemistry observed depends on the structure of the radical cation formed from the donor. As mentioned above, when this is incapable of fragmentation at the radical cation stage, back electron transfer (path *a*) ensues and the overall result is merely physical quenching, e.g. with *tert*-butylbenzene ($\Phi_{reac} = 1 \times 10^{-4}$).[4] When the donor contains a good potential leaving group at the benzylic position, as is the case with benzyltrimethylsilane, the radical cation undergoes cleavage to give the benzyl radical and a cation (in this case the silyl cation, see path *b*) with the solvent acting as a nucleophile.[5] A chemical reaction occurs with moderate efficiency ($\Phi_{reac} = 0.25$) involving combination of the benzyl radical with the DCN radical anion to finally give dihydronaphthalenedicarbonitriles **1** and **2**.

A different situation arises with alkylbenzenes having benzylic hydrogens. With toluene, for example, the main reaction ($\Phi_{reac} = 0.07$) results from proton exchange *within* the radical ion pair to give a radical pair. Radical coupling ensues and gives a different adduct, namely compound **3** (path *c*).[6] The difference is due to the fact that, in contrast to the desilylation case, proton transfer from a benzylic radical cation to the medium is slow (in a related case it has been shown that $k_{-SiMe3} \approx 200\ k_{-H}$),[6d] while direct proton transfer to the radical anion in the radical ion pair takes place efficiently. In neither case are benzyl radicals obtained as free and thus trappable species under these conditions (polar aprotic solvent such as acetonitrile) because they are generated near the DCN radical anion and invariably couple with it.



Scheme 1

A way to overcome this limitation would be to increase the stabilization of the radical ions through solvation so that fragmentation takes place at the free radical ion stage (path *d*). We have previously found that small amounts (0.1−0.5%) of protic additives such as water or methanol scarcely affected the product distribution.[6a] However, the reaction course changed when the reaction was carried out in neat protic solvents or acetonitrile containing a large

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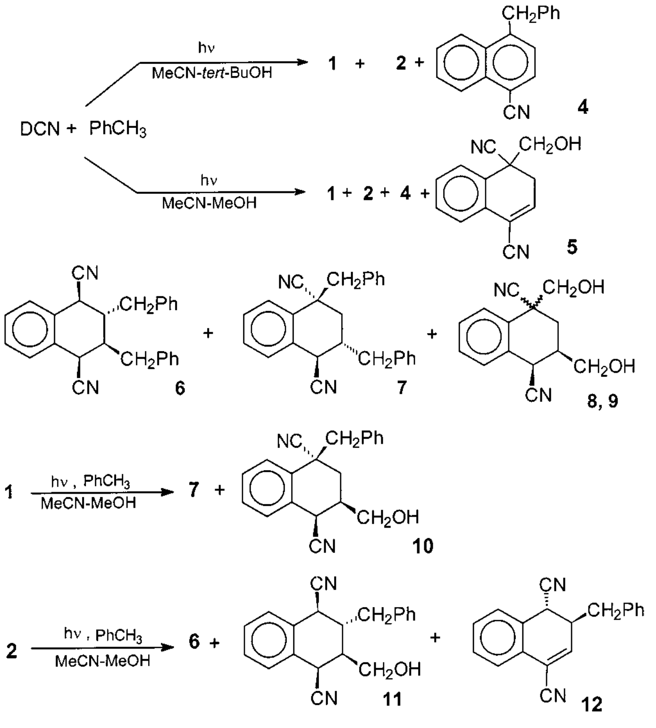
fraction of a protic co-solvent.[6c] The results presented herein show that under such conditions benzyl radicals not only add to DCN but also are trapped in the presence of nucleophilic alkenes. When the protic co-solvent has a hydrogen that can be abstracted, secondary radicals may be efficiently formed and trapped in turn. Thus, the present system represents a suitable model for assessing the potential of photoinduced electron transfer for the generation of radicals from hydrocarbons.

## Results

### Photochemistry of DCN/Toluene in MeCN/Alcohol Mixtures

As mentioned above, irradiation of DCN in the presence of 0.16 M toluene in neat MeCN gave the tetracyclic derivative **3** as the main product. In a MeCN/*t*BuOH (3:1) mixture, however, **3** was not formed, but rather 4-benzyl-1-naphthalenecarbonitrile (**4**), two dihydronaphthalenedicarbonitriles, the *cis*-2-benzyl- (**2**) and 1-benzyl- (**1**) derivatives, as well as a small amount of bibenzyl. When the reaction was repeated with a longer irradiation time (6 h), the product distribution did not change, showing that the dihydro derivatives **1** and **2** are stable under these conditions. Compounds **2** and **4** are minor products of the irradiation in MeCN.[6a]



Scheme 2

Irradiation of DCN/toluene in an MeCN/MeOH mixture (1:1) gave a more complex product mixture. When the reaction was terminated after 3 h, the DCN conversion was incomplete and some monoalkyl 1,2-dihydronaphthalene-1,4-dicarbonitriles could be isolated. These were the aforementioned benzyl derivatives **1** and **2**, plus the 1-(hydroxymethyl) derivative **5**. After 6 h, the DCN was fully consumed and, besides some bibenzyl, four products were isolated and characterized following chromatographic separation of the complex reaction mixture. All of them were dialkylated 1,2,3,4-tetrahydronaphthalene-1,4-dicarbonitriles (see Experimental Section for the structure identifications), specifically the 2,3-dibenzyl derivative **6**, the 1,3-dibenzyl analogue **7** (configuration at C-1 assumed supposing that the benzyl group is pseudoequatorial), and the two diastereoisomeric 1,3-bis(hydroxymethyl) derivatives **8** and **9**, having the same configuration at positions 3 and 4 and differing in the configuration at C-1.

In order to assess the possible roles of these alkyldihydronaphthalenes in the formation of the aforementioned dialkyltetrahydronaphthalenes, separate experiments were carried out. Thus, irradiation of the 1-benzyl derivative **1** in the presence of toluene in a 1:1 MeCN/MeOH mixture gave two main products, viz. the dibenzylated tetrahydronaphthalene **7** and the benzylhydroxymethyltetrahydro derivative **10** (Scheme 2).

Similar irradiation of the 2-benzyl derivative **2** also gave two tetrahydro derivatives, viz. compounds **6** and **11**, as well as the *trans* isomer of **2**, compound **12**.

The dihydro derivatives **1** and **2** absorbed the Pyrex-filtered light rather poorly, thus the above reactions were slow. On the other hand, irradiation at 254 nm in the absence of toluene led to ring-cleaved products via successive electrocyclic and sigmatropic rearrangements, as has been reported elsewhere.[7] DCN, on the other hand, proved to be photostable upon irradiation in either acetonitrile or MeCN/MeOH or MeCN/*t*BuOH mixtures when toluene was omitted.

### Photochemistry in the Presence of Alkenes Substituted with Electron-Withdrawing Groups

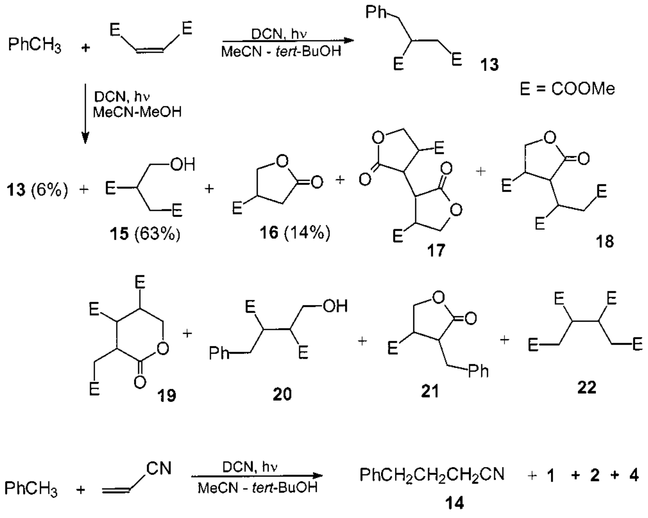
When the irradiation of DCN/0.16 M toluene in a MeCN/*t*BuOH (3:1) mixture was carried out in the presence of 0.15 M dimethyl maleate, the main product was dimethyl benzylsuccinate (**13**) accompanied by some bibenzyl (Scheme 3), while DCN-derived products were only found in trace amounts. The molar yield of succinate exceeded the amount of DCN used. Therefore, the yields given in Table 2 refer to the number of mols with respect to the number of mols of DCN. The same reaction was also carried out in the presence of acrylonitrile (0.5 M). In this case, both 4-phenylbutyronitrile (**14**) and the aforementioned naphthalenecarbonitriles **1**, **2** and **4** were obtained. Significantly, adducts **13** and **14** were not obtained in neat MeCN.

Irradiation of the DCN/toluene/dimethyl maleate system in MeCN/MeOH led to a variety of alkylated dimethyl succinates and related esters and lactones (Scheme 3), while no characterizable product containing the DCN moiety could be separated. Dimethyl 2-benzylsuccinate (**13**) constituted a minor fraction of the alkylated succinic esters obtained (6%). Most of the products (almost 90%) resulted from the

Table 1. Photoinduced alkylation of DCN and related nitriles in the presence of toluene (0.016 M)[a]

| Substrate | Solvent | Irradiation time | Products (% Yield) |
|---|---|---|---|
| DCN | MeCN | 3 h | **1** (tr), **2** (8), **3** (35), **4** (12)[a][b] |
| DCN | MeCN/*t*BuOH, 3:1 | 4 h | **1** (20), **2** (3), **4** (10) |
| DCN | MeCN/MeOH, 1:1 | 3 h | **1** (6), **2** (tr), **6−9** (tr), **5** (30) |
| DCN | MeCN/MeOH, 1:1 | 6 h | **6** (10), **7** (8), **8** (12), **9** (11) |
| **1** | MeCN/MeOH, 1:1 | 15 h | **7** (12), **10** (20) |
| **2** | MeCN/MeOH, 1:1 | 15h | **6** (15), **11** (8), **12** (15) |

[a] In all experiments, a small amount of bibenzyl was formed. − [b] See ref.[3b]



Scheme 3

incorporation of a hydroxymethyl rather than a benzyl group; in particular, 2-hydroxymethylsuccinate (**15**) alone accounted for some 63% of the alkylation products and four other products resulted from addition of this group. These were the corresponding lactone (**16**) (14%) and a dimer of the latter compound (**17**), as well as two lactones derived from 2-hydroxymethyl-3,4-dicarboxyladipic acid, the structures of which were determined by NMR analysis. Both were obtained as diastereoisomeric mixtures with one diastereoisomer predominating. The $^1$H- and $^{13}$C-NMR spectra of these diastereomers were similar, except for the coupling constants of the methylene group near the oxygen and the chemical shifts of lactone carbonyl groups. The observed differences were in accordance with cyclic structures of five (**18**) and six (**19**) atoms (see Experimental Section for details). Finally, two compounds containing both the hydroxymethyl and the benzyl radical accounted for the remaining 4%. These were dimethyl 2-benzyl-3-hydroxymethylsuccinate (**20**) and the corresponding lactone (**21**). A considerable amount of maleate was reduced rather than alkylated, yielding tetramethyl 3,4-dicarboxyadipate (**22**, the molar amount of this product corresponded to ca. one-third of the alkylated derivatives). With respect to the starting amount of DCN, the global molar yield of these esters considerably exceeded unity (3.5).

## Discussion

In all of the above photoreactions, the primary process involves singlet-excited DCN and toluene. Indeed, no reaction takes place upon irradiation of DCN in MeCN or in MeCN/alcohol mixtures. Under the conditions of the experiments, the DCN fluorescence is almost completely quenched by toluene ($k_q = 1.8 \times 10^7$ $\text{M}^{-1}\text{s}^{-1}$).[6a] The primary step involves photoinduced electron transfer and is significant only when $\Delta G_{\text{ET}} \leq 0$ ($\Delta G_{\text{ET}}$ is calculated to be almost thermoneutral with toluene as the donor). Weak donors such as alcohols do not significantly quench the DCN singlet ($k_q < 1 \times 10^6$ $\text{M}^{-1}\text{s}^{-1}$). Quenching by toluene leads to a radical ion pair. In a polar aprotic solvent such as MeCN, the reaction occurs, as has previously been demonstrated, at the geminate radical ion pair (or strongly polarized exciplex, if one prefers to envisage it in this way) and the main product is the tetracyclic adduct **3**. A protic, nucleophilic solvent such as an alcohol changes the course of the reaction by stabilizing the radical ions and thereby facilitating diffusion out of the cage, although as mentioned previously the alcohol has to constitute a significant fraction of the medium for such an effect to be observed. Alcohols have little effect on the DCN radical anion, which, like related radical anions of aromatic nitriles, is quite persistent in protic solvents[8] (stronger acids protonate $\text{DCN}^{-\cdot}$; e.g. with 0.01 M trifluoroacetic acid the main product is 1,2-dihydronaphthalenedicarbonitrile).[3b] However, they play a role in assisting deprotonation of the toluene radical cation, a reaction that is known to occur only as a second-order process in related substrates.[6d]

This is apparent in the reaction in MeCN/*t*BuOH. In this case, the tetracyclic adduct **3** is no longer formed and the main chemical path involves out-of-cage deprotonation of toluene to yield benzyl radicals. The yield of bibenzyl is somewhat increased, but the main fate of the radicals is addition to the persistent DCN radical anion to give the benzylated dihydronaphthalenes **1** and **2** or to ground state DCN to give the benzylmononitrile **4**.

Addition of an electrophilic alkene such as dimethyl maleate results in efficient trapping of the radicals to give succinate **13**. The successful benzylation of the maleate under these conditions may be of some synthetic interest, in view of the fact that product **13** has not previously been obtained via a radical path and in the present method the radicals

Table 2. Photoinduced alkylation of electrophilic alkenes in the presence of DCN and toluene

| Alkene | Solvent | Irradiation time | Products (mol per mol of DCN) |
|---|---|---|---|
| Dimethyl maleate | MeCN/*t*BuOH, 3:1 | 4 h | **13** (2.5) |
| Acrylonitrile | MeCN/*t*BuOH, 3:1 | 4 h | **1** (0.1), **2** (tr), **3** (0.05), **14** (0.8) |
| Dimethyl maleate | MeCN/MeOH, 1:1 | 4 h | **13** (0.24), **15** (2.42), **16** (0.53), **17** (0.23), **18** (0.14), **19** (0.09), **20** (0.05), **21** (0.11), **22** (1.57) |

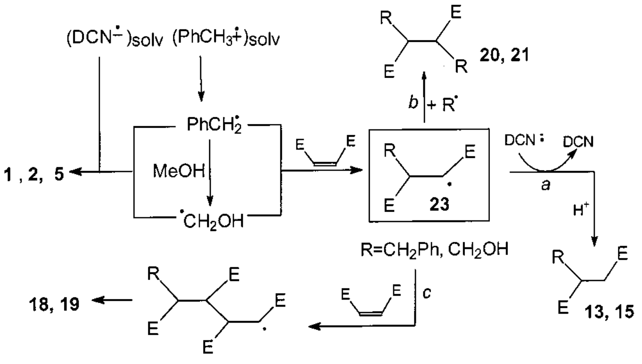
are generated directly from toluene under extremely mild conditions. With a less efficient trap, such as acrylonitrile, both the DCN and alkene adducts are formed, indicating that trapping by the alkene is in this case too slow to completely overcome the diffusion-controlled coupling with the DCN radical anion, but at the same time suggesting that the scope of the reaction can be extended somewhat.

The radical alkylation of electrophilic alkenes through photoinduced electron transfer (PET) and radical cation fragmentation has previously been demonstrated for various alkyl radicals, but it has never been realized with the more stable benzyl radicals.[2a,9] In an aprotic solvent, these couple with the nitrile radical anion, even when produced from a fast-cleaving benzylic donor such as benzyltrimethylsilane (Scheme 1, path *b*).[5] The present study shows that the benzylation of electrophilic alkenes can be effected in protic solvents, apparently by favouring escape out of the cage of the radical ions, so that the radical is no longer produced in the vicinity of the radical anion (path *c*) but rather from the free solvated species (path *d*).

Generation of radicals by the PET method is sensitive to the substrate oxidation potential, and not to the bond strength. Thus, benzyl radicals can be generated from alkylbenzenes by DCN-sensitization under conditions where alcohols do not react due to the very large difference in the oxidation potential of such substrates, $E_{ox} = 2.4$ V *vs.* SCE for $PhCH_3$ and > 3.5 V for MeOH. This is reflected in the difference in the quenching rate constants (by a factor > 20, see above). This differentiates the present method from radical generation by atom transfer, e.g. by triplet ketones, where the difference is much smaller, e.g. the rate constants for the reaction of benzophenone triplet with toluene and methanol are $k_H = 5$ and $2 \times 10^5\ \mathrm{M^{-1}s^{-1}}$,[10] respectively, reflecting the relatively small difference in the BDEs (88 *vs.* 94 $\mathrm{kcal^{-1}\ M^{-1}}$).[11] With very strong photochemical oxidants such as 1,2,4,5-benzenetetracarbonitrile, oxidation of alcohols and the ensuing C−H deprotonation are, however, possible.[12]

In the presence of a large amount of an alcohol as a co-solvent, hydrogen abstraction from the alcohol by the benzyl radical competes with addition (Scheme 4). In this indirect way, hydroxyalkyl radicals are generated, which can then undergo addition to electrophilic alkenes as illustrated here by the reaction with dimethyl maleate. The latter process leads to various adducts, most of which (94%) incorporate the hydroxymethyl group (**15** and the corresponding lactone **16**). Hydroxymethylation of maleate has previously been achieved by Eu(III)-PET sensitization.[13]

The present alkylation reactions can reasonably be terminated by back electron transfer from the DCN radical anion to the radical adduct **23** to give an anion followed by protonation of the latter (path *a* in Scheme 4), or alternatively by hydrogen transfer to the adduct radical by the methanol or toluene. The termination step is relatively inefficient. In the case of methanol, for example, this is shown by the fact that ca. 17% of the adduct radical **23** reacts along paths other than hydrogen abstraction, viz. dimerization to give **17**, cross-coupling with a benzyl radical to give **20** and **21** (path *b* in Scheme 4), or addition of a further maleate molecule to give products **18** and **19** (path *c* in Scheme 4). Under these conditions, DCN is consumed via an undetermined reductive path.



Scheme 4

However, the alkylation of electrophilic alkenes is more efficient (e.g. by a factor of 2.5 or 3.8 for the reactions of dimethyl maleate in MeCN/*t*BuOH and MeCN/MeOH, respectively) than DCN consumption, showing that, at least in part, DCN acts as a regenerated sensitizer as outlined above.

In the absence of the trap, the hydroxymethyl radicals add to the nitrile in competition with the benzyl radicals. The reaction involves some coupling with $DCN^{-\cdot}$ as discussed above and leads to the alkylated dihydronaphthalenes **1**, **2** and **5**. In turn, these can be further alkylated through a secondary photochemical reaction, as shown by separate experiments on such derivatives, where addition of both benzyl and hydroxymethyl radicals again takes place. Along with **6** and **7**, tetrahydronaphthalenes containing two different alkyl groups such as **10** and **11** are obtained upon separate irradiation of **2** and **1**. These were not isolated starting from DCN. This difference is apparently related to the different absorbing species. In the direct experiment, the light (medium-pressure mercury arc with Pyrex glass filter) is absorbed by DCN and the second alkylation is also a DCN-photosensitized reaction with the mono-alkylated derivative acting as a radical trap. Dihydronaphthalenes **1** and **2** absorb poorly at these wavelengths, and this may lead to a different ratio of the benzyl and hydroxymethyl radicals when starting from preformed **1** and **2**. It is interesting to note that the second alkylation of dihydronaphthalenes **1** and **2** takes place only in the presence of methanol, while tetrahydronaphthalenes are not formed in MeCN/*t*BuOH, even after prolonged irradiation. This difference highlights a specific effect of methanol which, besides solvating radical ions, increases both the amount and the lifetime of benzyl radicals such that trapping by the unsaturated nitrile moiety in compounds **1** and **2** becomes possible.

## Conclusion

In conclusion, this work highlights some of the characteristics of the PET-sensitized method for the generation of alkyl radicals. The first step involves oxidation of the substrate by the excited sensitizer. This is not too stringent a requirement, as shown here where a moderate electron donor such as toluene and a moderate electron acceptor such as DCN singlet are used. In the present case, electron transfer is thermoneutral, although this step is sufficiently fast to lead to a reasonable reaction. More importantly, this requirement makes the method flexible, since the reduction potential of the oxidant can be varied by choosing an appropriate sensitizer e.g. among aromatic nitriles or esters. Thus, it is possible to carry out a selective oxidation, in the present case differentiating an aromatic hydrocarbon from an alcohol. This makes PET-sensitization a versatile method for the generation of radicals, more so than thermal redox reactions or hydrogen transfer reactions.

One peculiar factor that must be taken into account in photochemical reactions is the competition between the chemical reaction, viz. radical cation cleavage, and back electron transfer. In contrast to desilylation, for example, deprotonation is a moderately effective process. Whether it occurs in-cage at the radical ion pair stage or in the medium from the solvated free radical ion (path c *vs.* path d) depends on the choice of the solvent, viz. on the presence of an alcohol as co-solvent. In the latter case, there exists the possibility of benzylating electrophilic alkenes starting directly from the hydrocarbon. If the alcohol has an available α-hydrogen, hydroxyalkylation of the alkene through a secondary hydrogen transfer step ensues. In the absence of traps, polysubstituted reduced nitriles are obtained.

## Experimental Section

**General Remarks:** 1,4-Naphthalenedicarbonitrile was prepared and purified as described previously. The photochemical reactions were performed on Ar-purged solutions (100 mL) of DCN (120 mg, 0.67 mM) containing toluene (1.5 g, 16.3 mM), which were irradiated in an immersion well apparatus fitted with a Pyrex glass filter using a 150 W medium-pressure mercury arc lamp. Irradiations of the dihydronaphthalenes **1** and **2** were carried out similarly, as were the reactions in the presence of acrylonitrile and dimethyl maleate. Workup of the photolysates involved concentration in vacuo followed by column chromatographic separation using Merck type 60 (230−400 mesh) silica gel, eluting with cyclohexane/ethyl acetate mixtures of increasing polarity. Conditions and results are reported in Tables 1 and 2. $^1$H- and $^{13}$C-NMR spectra were recorded with a Bruker AC 300 spectrometer. Chemical shifts are reported relative to TMS as an internal standard. The structures were deduced from the results of $^1$H, $^{13}$C, DEPT-135 and H,H-COSY experiments.

Compounds **1**, **2**, **3**, **4**, **5**, **12**, **13**, **14**, **15**, **16**, and **22** have been reported previously; the spectroscopic properties of these materials were identical to the reported data.

**2,3-Bis(phenylmethyl)-1,2,3,4-tetrahydro-1,4-naphthalenedicarbonitrile (6):** M.p. 157−157.5 °C (methanol). − The stereochemistry was assigned on the basis of the coupling constants in the $^1$H-NMR spectrum. 1-H is pseudoaxial and *trans* to 2-H ($J$ = 10 Hz), which is axial in relation to 3-H ($J$ = 10 Hz); 4-H is *cis* to 3-H ($J$ = 4.5 Hz). − $^1$H NMR (CDCl$_3$): δ = 2.35 (tt, $J$ = 10, $J$ = 2 Hz, 1 H, 2-H), 2.45 (m, 1 H, 3-H), 2.77 (dd, $J_{AB}$ = 13.5, $J$ = 10 Hz, 1 H) and 3.27 (dd, $J_{AB}$ = 13.5, $J$ = 5 Hz, 1 H, 3-CH$_2$), 3.65 (d, $J$ = 4.5 Hz, 1 H, 4-H), 4.15 (d, $J$ = 2 Hz, 2 H, 2-CH$_2$), 4.41 (d, $J$ = 10 Hz, 1 H, 1-H), 7.3 (m, 14 H). − $^{13}$C NMR (CDCl$_3$): δ = 31.6, 33.3, 34.6, 35.8, 38.4, 41.2, 43.6, 58.7, 118.6, 120.1, 126.9, plus the aromatic signals.

**1,3-Bis(phenylmethyl)-1,2,3,4-tetrahydro-1,4-naphthalenedicarbonitrile (7):** M.p. 188−189 °C (methanol) − $^1$H NMR (CDCl$_3$): δ = 2.05 and 2.28 (AB part of ABX system, 2 H, 2-H), 2.43 (m, 1 H, 3-H), 3.15 (AB system, 2 H), 3.89 (AB part of an ABX system, 2 H), 4.13 (d, $J$ = 10.5 Hz, 1 H, 4-H), 7.3 (m, 14 H).

**1,3-Bis(hydroxymethyl)-1,2,3,4-tetrahydro-1,4-naphthalenedicarbonitrile (8 and 9):** Two diastereoisomers were obtained and separated. These had the same configuration at C-3 and C-4 ($J_{4,3}$ = 11.5 Hz in each case), but opposite configurations at C-1. − (**8**): M.p. 156−156.5 °C (methanol). − $^1$H NMR (CDCl$_3$): δ = 2.1 (d, $J_{AB}$ = 14 Hz, 1 H, 2-H), 2.4 (m, 1 H, 3-H), 3.77 (dd, $J_{AB}$ = 14, 1 H, 2-H), 3.82 (2 H, 1-CH$_2$), 4.28 (d, $J$ = 11.5 Hz, 1 H, 4-H), 4.3 (t, $J$ = 5 Hz, exchangeable, 1-OH), 4.32 (m, 2 H, 3-CH$_2$), 5.1 (t, $J$ = 6 Hz, exchangeable, 3-OH), 7.45 (m, 2 H), 7.6 (m, 2 H). − (**9**): M.p. 167−167.5 °C (methanol) − $^1$H NMR (CDCl$_3$): δ = 2.0 (d, $J_{AB}$ = 13 Hz, 1 H) and 2.58 (dd, $J_{AB}$ = 13, $J$ = 3 Hz, 1 H, 2-CH$_2$), 2.32 (m, 1 H, 3-H), 3.88 and 4.22 (AB system, 2 H, 1-H), 3.94 (m, 2 H, 3-CH$_2$), 4.28 (d, $J$ = 11.5, 1 H, 4-H), 4.32 (t, $J$ = 5 Hz, exchangeable, 1 H, 1-OH), 4.9 (t, $J$ = 6 Hz, exchangeable 1 H, 3-OH), 7.45 (m, 2 H), 7.6 (m, 1 H), 7.72 (m, 1 H).

**3-Hydroxymethyl-1-phenylmethyl-1,2,3,4-tetrahydro-1,4-naphthalenedicarbonitrile (10):** The stereochemistry was established on the basis of the couplings in the $^1$H-NMR spectrum: 4-H and 3-H are *cis* with 4-H in a pseudoaxial position ($J_{4,3}$ = 5 Hz); the C-1 configuration is the same as that in **2**. Thick oil. − $^1$H NMR (CDCl$_3$): δ = 2.05 (AB part of an ABX system, 2 H, 2-H), 2.43 (m, 1 H, 3-H), 2.97 and 3.17 (AB sytem, 2 H, CH$_2$Ph), 3.79 (m, 2 H, CH$_2$OH), 4.05 (d, $J$ = 5 Hz, 1 H, 4-H), 7.3 (m, 9 H).

**3-Hydroxymethyl-2-phenylmethyl-1,2,3,4-tetrahydro-1,4-naphthalenedicarbonitrile (11):** Thick oil. − $^1$H NMR (CDCl$_3$): δ = 2.58 (m, 1 H) and 2.62 (m, 1 H, 2-H and 3-H), 3.15 (AB part of an ABX system, 2 H, CH$_2$Ph), 4.0 (d, $J$ = 5 Hz, 1 H, 1-H), 4.05 (AB part of an ABX system, 2 H, CH$_2$OH), 4.25 (d, $J$ = 5 Hz, 1 H, 4-H), 7.4 (m, 9 H).

**Dimer 17:** Oil obtained as a chromatographic fraction; mixture of two diastereoisomers. The reported data relate to the most abundant diastereomer. − $^{1}$H NMR ($CDCl_3$): $\delta = 3.38$ (d, $J = 11$ Hz, 1 H, 3-H), 3.78 (s, 3 H), 4.05 (dt, $J = 11$ Hz, $J = 9$ Hz, 1 H, 4-H), 4.38 (t, $J = 9$ Hz, 1 H) and 4.43 (t, $J = 9$ Hz, 1 H, 5-$CH_2$). − $^{13}$C NMR ($CDCl_3$): $\delta = 41.0$, 42.6, 52.7, 66.8, 170.1, 175.5.

**Dimethyl 2-[3-(4-Methoxycarbonyl-1,2,3,4-tetrahydro-2-furanonyl)]-3-butanedioate (18):** Oil. The cyclic lactone structure with a five-membered ring was deduced on the basis of the following NMR data: the two hydrogens of the methylene bonded to the oxygen show the same coupling (9 Hz) with 4-H; in the $^{13}$C spectrum, the lactone carbonyl group appears at $\delta = 175$, in accordance with literature data showing an upfield shift for such a five-membered ring. The product was found to be a mixture of three diastereoisomers with one predominating. The reported data relate to the principal diastereoisomer. − $^{1}$H NMR ($CDCl_3$): $\delta = 2.76$ (dd, $J_{AB} = 16$, $J = 7$ Hz, 1 H) and 3.0 (dd, $J_{AB} = 16$, $J = 7$ Hz, 1 H, 3-$CH_2$), 3.28 (dd, $J = 3$, 10 Hz, 1 H, 3′-H), 3.5 (m, 1 H, 2-H), 3.55 (m, 1 H, 4-H), 3.72 (s, 3 H), 3.74 (s, 3 H), 3.78 (s, 3 H), 4.3 (t, $J = 9$ Hz, 1 H) and (t, $J = 9$ Hz, 1 H, 5-$CH_2$). − $^{13}$C NMR ($CDCl_3$): $\delta = 38.8$, 40.0, 43.3, 43.5, 51.9, 52.4, 52.6, 66.9, 170.7, 171.5, 172.1, 174.9.

**Methyl 2-(2*H*-4,5-Dimethoxycarbonyl-3,4,5,6-tetrahydro-2-pyranoyl)ethanoate (19):** In this case, in comparison with **18**, the two hydrogens of the methylene bonded to the oxygen show two different coupling constants with 5-H (6 and 12 Hz). In the $^{13}$C spectrum, the lactone carbonyl group appears at $\delta = 172$, a value typical for a six-membered ring. The product was found to consist of a mixture of two diastereoisomers. The reported data relate to the principal diastereoisomer. − $^{1}$H NMR ($CDCl_3$): $\delta = 2.4$ (dd, $J_{AB} = 17$, $J = 6$ Hz, 1 H) and 2.9 (dd, $J_{AB} = 17$, $J = 7$ Hz, 1 H, $CH_2COOMe$), 3.24−3.45 (m, 2 H, 5-H and 3-H), 3.65 (m, 1 H, 4-H), 3.7 (s, 3 H), 3.74 (s, 3 H), 3.76 (s, 3 H), 4.4 (dd, $J_{AB} = 11$, $J = 6$ Hz, 1 H) and 4.6 ($J_{AB} = 11$, $J = 12$ Hz, 1 H, 6-$CH_2$). − $^{13}$C NMR ($CDCl_3$): $\delta = 31.9$, 37.5, 41.7, 42.4, 51.8, 65.0, 170.0, 171.0, 171.2, 171.8.

**Dimethyl 2-Hydroxymethyl-3-phenylmethylbutanedioate (20):** Chromatographic fraction containing some **16**. − $^{1}$H NMR ($CDCl_3$): $\delta = 2.9$ (m, 2 H), 3.0 (1 H) and 3.9 (1 H, AB part of an ABX system, $PhCH_2$), 3.1 (m, 1 H, 3-H), 3.6 (s, 3 H, OMe), 3.75 (s, 3 H, OMe). − $^{13}$C NMR ($CDCl_3$): $\delta = 35.3$, 46.2, 47.8, 51.8, 51.9, 61.1, 128.8, 128.3, 126.5, 138.3, 173.4, 173.9.

**Methyl 3-Phenylmethyl-2,3,4,5-tetrahydro-2-furanonyl-4-carboxylate (21):** The lactone carbonyl group gives rise to a signal at $\delta = 176$ in the $^{13}$C-NMR spectrum, a value characteristic for a five-membered ring. − $^{1}$H NMR ($CDCl_3$): $\delta = 3.1$ and 3.2 (AB part of ABX system, 2 H, $PhCH_2$), 3.15 (m, 1 H, 4-H), 3.25 (m, 3-H), 3.6 (s, 3 H, OMe), 4.1 (AB part of an ABX system, 2 H, 5-$CH_2$). − $^{13}$C NMR ($CDCl_3$): $\delta = 34.6$, 44.4, 52.4, 67.0, 171.2, 176.2.

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