Photochemistry of some trialkylsilyloxybenzylidenemalonic acid derivatives. C–Si bond fragmentation in a polarized excited state

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Photolysis of 3-(*tert*-butyldimethylsilyloxyphenyl)methylenemalonodinitrile (2) in a polar medium leads to C–Si cleavage *via* the polarized singlet excited state. The thus formed *tert*-butyl radicals diffuse out of cage and are trapped by further molecules of 2. In contrast, the photochemical alkylation of benzylidenemalonodinitrile by *tert*-butyldimethylsilyl phenyl ether occurs *via* the radical cation and requires phenanthrene sensitization. In an apolar solvent, 2 undergoes only a slow dimerization and gives two (one main) cyclobutanes. Photoinduced cleavage is not observed neither with the corresponding diester nor with the 2-silyloxy analogue of 2 (the lowest excited singlet of the latter compound is an ICT state).

A new method for the generation of alkyl radicals from unconventional substrates is based on the fragmentation of a single bond [eqn. (1)][1–4] in radical ions, in turn obtained by

$$DX^{\bullet +} \longrightarrow D^{\bullet} + X^{+} \quad (1)$$

photoinduced electron transfer [eqn. (2)][5–10] competitively with back electron transfer.

$$AZ^{*} + DX \text{ or } AZ + DX^{*} \longrightarrow AZ^{\bullet -} + DX^{\bullet +} \quad (2)$$

Several groups of such reactions have been recently discovered, and radical alkylation under these conditions is successful.[11] It appeared of interest to us to test whether the presence of both a donor and an acceptor moiety within the same molecule would facilitate photofragmentation. Intramolecular photoinduced electron transfer has been previously studied, both in systems containing a donor and an acceptor moiety separated by a non-conjugating 'spacer' [eqn. (3)],[12–15] and in conjugated systems [eqn. (4)].[16,17] However, such models have been studied up to now almost only from the photophysical point of view.

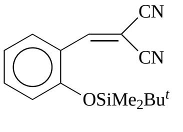
$$A^{*}\!\sim\!D \longrightarrow A^{\bullet -}\!\sim\!D^{\bullet +} \quad (3)$$

$$A^{*}\!-\!D \longrightarrow A^{\bullet -}\!-\!D^{\bullet +} \quad (4)$$

We now report a chemical study concerning a photofragmentation reaction in aromatic derivatives of the latter type.

Results

We chose as a model some derivatives of trialkylsilyloxybenzylidenemalonic acid. These incorporated both a donating moiety with a fragmentable bond (C–Si),[8,18–20] and an accepting moiety that would also function as a radical trap, the alkylidenemalonic group.[19] These materials were prepared by Knoevenagel condensation of the appropriate hydroxy aldehydes with either malonodinitrile or diethyl malonate followed by silylation.



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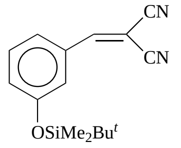

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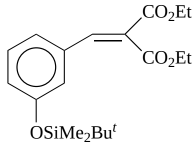

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Spectroscopy

The absorption spectra of 2- and 3-(*tert*-butyldimethylsilyloxy)benzylidenemalonodinitriles (**1** and **2**) as well as that of the corresponding 3-substituted diethyl malonate **3** in cyclohexane and in acetonitrile are shown in Fig. 1(*a*) and (*b*). Compound **2** showed a blue fluorescence, while the emission of isomeric **1** was very weak [Table 1, Fig. 1(*b*)]. The shape of the fluorescence spectrum of **2** showed no significant concentration dependence, while it was strongly shifted in polar solvents [Fig. 1(*b*)]. The emission was quenched both by benzylidenemalonodinitrile (**4**) and by phenyl *tert*-butyldimethylsilyl ether (**5**) (see Table 1). The absorbance spectrum of compound **4** is also shown for comparison [Fig. 1(*c*)]. The silyl ether **5** has the

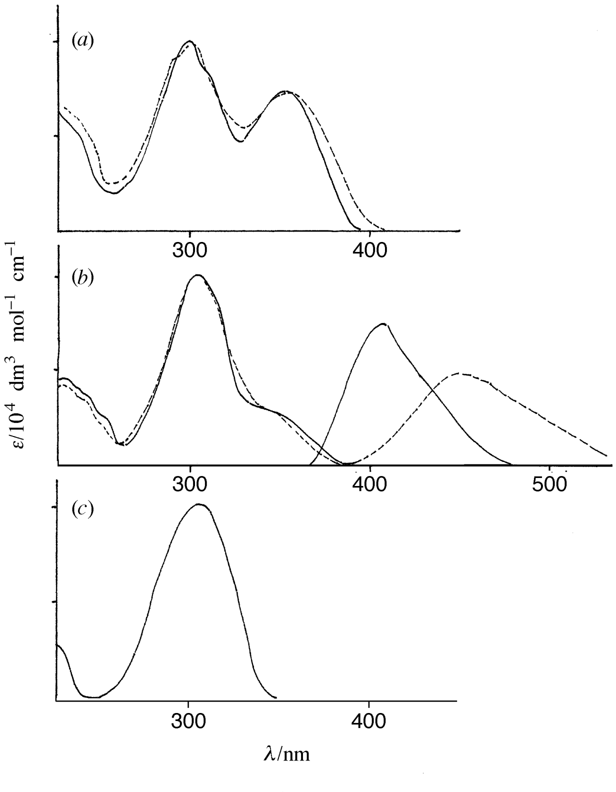


Fig. 1 Absorption spectrum of dinitriles **1** (*a*), **2** (*b*) and **4** (*c*) in cyclohexane (——) and in acetonitrile (– – –). The fluorescence spectra of compound **2** (arbitrary units) are also reported.

Table 1 Spectroscopic characteristics of the benzylidenemalonic acid derivatives **1**, **2** and **3**

		Absorption[a]		Fluorescence			Fluoroescence quenching
Substrate	Solvent	λ_{max}/nm	λ_{00}/nm	λ_{max}/nm	λ_{00}/nm	Stokes shift/cm^{-1}	K_{sv}/dm^3 mol^{-1}
1	Cyclohexane	352	395	405	380	3700	
1	MeCN	355	410	430	400	5000	
2	Cyclohexane	350	385	407	365	4000	K_{sv}(**4**) = 1.5, K_{sv}(**5**) = 1.5
2	MeCN	*ca.* 345	385	450	390	6700	K_{sv}(**4**) = 2, K_{sv}(**5**) = 1.5
3	Cyclohexane	318	335	350	328	2800	
3	MeCN	325	348	395	340	4500	

[a] Longest wavelength absorption maximum (λ_{max}) for compound **1**, or evaluated by deconvolution of the shoulder on the red edge of the band in the case of compounds **2** and **3**; λ_{00} indicates the beginning of the absorption or, respectively, of the fluorescence.

Table 2 Results from the photochemical reactions[a]

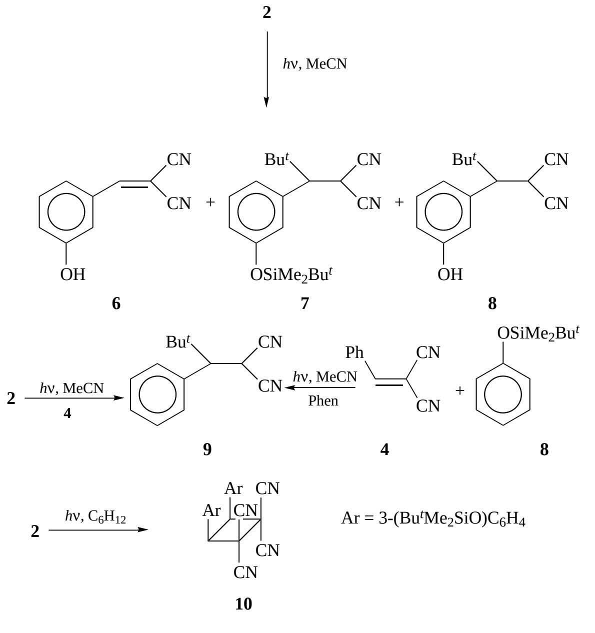
Entry Number	Substrate(s)	Solvent	Additive	Irradiation *t*/h	Substrate converted (%)	Products (% yield)
1	**2**, 0.01 M	MeCN		10	95	**6** (43), **7** (35), **8** (17)
2	**2**, 0.01 M	MeCN		4	40	**6** (20), **7** (17), **8** (2)
3	**2**, 0.01 M	Cyclohexane		45	60	**10** (40)
4	**2**, 0.01 M	MeCN	Phen, 0.01 M	10	90	**6** (40), **7** (31), **8** (15)
5	**2**, 0.01 M; **4**, 0.1 M	MeCN		10	90	**6** (72), **7** (2), **9** (55)
6	**2**, 0.01 M; **5**, 0.1 M	MeCN		10	95	**6** (45), **7** (37), **8** (13)
7[b]	**4**, 0.05 M; **5**, 0.1 M	MeCN	Phen, 0.01 M	30	15	**9** (10)
8[c]	**5**, 0.1 M	MeCN		30	<3	

[a] By irradiation at 320 nm, unless otherwise noted. [b] No detectable reaction omitting Phen. [c] By irradiation at 254 nm.

absorbance maximum at 268 nm and the emission maximum at 295 nm (unaffected by the solvent).

Photochemical reactions

Irradiation of the dinitrile **1** in degassed acetonitrile caused no change. On the other hand, isomeric **2** reacted under the same conditions and gave three products (Scheme 1, Table 2). One of these was the phenol corresponding to the starting material (**6**). The other two had lost the conjugated double bond and were identified from their spectroscopic and analytical properties as the saturated silyloxyphenyl dinitrile **7** and the corresponding phenol **8**. The diester **3** showed no significant photoreactivity under these conditions.



Scheme 1

The photoreaction of compound **2** (1×10^{-2} M) was further investigated. The proportion of product **7** with respect to the non-silylated analogue **8** was larger at the beginning of the irradiation (Table 2, entry 2). The reaction was little affected by the starting material concentration in the range 0.03–0.15 M. It occurred in the same way in the presence of phenanthrene (3×10^{-3} M) (entry 4). Addition of several radical traps, *viz.* acrylonitrile, diethyl maleate, diethyl benzylidenemalonate or 2-phenylpropylidenemalonodinitrile, all 0.1 M, did not affect the reaction, giving again products **6**–**8**. Addition of 0.1 M benzylidenemalodinitrile (**4**), however, quenched the formation of adduct **7** and mainly gave a different compound recognized as the saturated nitrile **9** (entry 5). Irradiation of **2** in the presence of 0.1 M phenyl *tert*-butyldimethylsilyl ether (**5**) gave the same products as above, with some increase of the yield of the silylated adduct **7** with respect to **6** and **8** (entry 6).

As for the solvent dependence, the same reaction observed in acetonitrile occurred also in acetone, although at a lower rate, but not in either dichloromethane or cyclohexane. Upon prolonged irradiation in cyclohexane a reaction occurred. However, this followed a different course (entry 3). A single product was obtained from chromatographic work-up and was shown to be a dimer with a cyclobutane structure. No firm evidence was obtained about the stereochemistry, but the downfield resonance of the cyclobutane proton and comparison with known models[21,22] suggested that the phenyl groups were in the 1,2-*cis* arrangement (**10**). The presence of a minor amount of a second dimer was inferred from the presence of a further cyclobutane proton (at a higher field, see Experimental) in the spectrum of the photolysate, but this was not separated.

A comparable intermolecular example was also explored. Thus, irradiation of benzylidenemalonodinitrile (**4**, 0.05 M) and phenyl *tert*-butyldimethylsilyl ether (0.1 M) in MeCN caused no reaction, but in the presence of 0.01 M phenanthrene the saturated nitrile **9** was formed in a slow reaction (entry 7). Furthermore, prolonged irradiation of phenyl silyl ether **5** (at 254 nm, entry 8) caused no appreciable decomposition of the substrate.

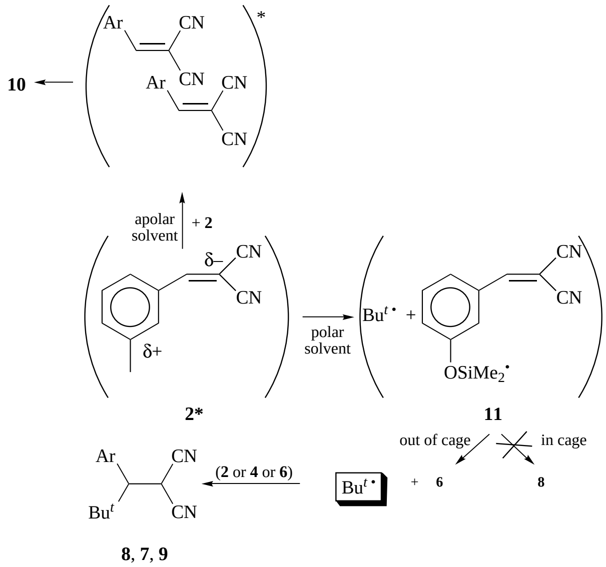
Discussion

The lowest singlet excited states of the presently considered silyloxybenzylidene derivatives of malonic acid and malonodinitrile have an internal charge transfer character. Comparison of the absorption spectrum of benzylidenemalodinitrile **4** with that of its 3-silyloxy derivative **2** shows that the two spectra are virtually superimposable in the 270–340 nm region, where the strong $\pi\pi^*$ band typical of arylalkenes, and in particular of cynnamic acid derivatives, appears. Compound **2**, however, further shows a shoulder on the long-wavelength side of that band. This can be deconvoluted to show a new band at 350 nm [Fig. 1(*b*), Table 1]. The absorption spectrum shows a minor dependence on solvent polarity.

As for the fluorescence, compound **2** emits in the visible; the emission shows both a marked red shift with polar solvents and a relevant Stokes shift with respect to the absorption. For comparison, one should take into account the fact that benzylidenemalonodinitrile does not emit and phenyl *tert*-butyldimethylsilyl ether, like phenol, absorbs and emits in the UV (absorbance, $\lambda_{\mathbf{max}}$ 268 nm, fluorescence, $\lambda_{\mathbf{max}}$ 295 nm).

The same considerations can be applied to the spectra of the 3-silyloxy diester **3**, which are markedly blue shifted with respect to dinitrile **2**, and show a lower Stokes shift.

Thus, although no formal zwitterionic mesomeric structures can be drawn, internal charge transfer over the conjugated system occurs (see formula **2*** in Scheme 2). The relaxed singlet excited state shows considerable charge separation, as shown by the red shift of the emission (not of the absorption) induced by a polar medium.



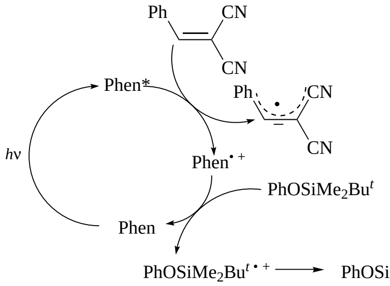
Scheme 2

Indeed, the chemistry of this excited state is strongly environment dependent. In an apolar solvent a slow photodimerization takes place. This is another example of the well known dimerization of cynnamic acid derivatives, often an inefficient reaction in solution[23–25] (while it is efficient in the solid state). As in related cases, the inefficiency is due both to steric crowding and to fast deactivation of the excited state through rotation around the C–C double bond. The stereochemistry assigned to the main product **10** on the basis of analogy of the NMR signals[21,22] is also the one expected from maximum superimposition of the π systems at the exciplex stage (Scheme 2).

In a polar medium, however, compound **2** is photodecomposed and the alkylated derivatives **7** and **8** are formed. We suggest that the primary step is homolytic cleavage of the Si–C bond (*vide infra*). The energy of $\mathbf{2}^{1}$*, evaluated from the crossing point of absorption and emission spectra, is 76 kcal mol^{-1} (1 cal = 4.184 J) both in cyclohexane and in MeCN. This is close to that expected for the Si–Bu^t bond in this compound (compare Me$_3$Si–Bu^t, 83 kcal mol^{-1},[26] and take into account the effect of the phenoxy group). However, in order that fragmentation takes place at a sufficient rate to compete with physical deactivation of the excited state, the role of the polarity of the medium in favouring internal charge transfer is determining. One can rationalize this result with reference to intermolecular electron transfer. Excitation of **2** involves electron withdrawal from the Si–C bond, which thus acquires a partial single electron bond character. The radical cations of silanes and silyl ethers are known to undergo fragmentation of the C–Si bond,[18] and this also suggests that a polarized excited state such as that of **2** undergoes fragmentation of the C–Si bond, particularly when charge separation in the relaxed excited state is favoured by a polar medium. The cleavage occurs selectively and gives the most stable (*tert*-butyl) radical.

Loss of dimethylsilylene from the phenoxydimethylsilyl radical **11** eventually gives phenol **6**. The *tert*-butyl radical adds to the activated >C=C(CN)$_2$ moiety. This can occur in two ways, by in cage coupling with radical **11** (finally yielding **8**) and after diffusion out of cage (yielding **7** from **2** and **8** from **6** which accumulates during the progress of the photochemical desilylation, see Scheme 2). The latter path predominates as shown by two pieces of evidence. The first is the larger proportion of the silylated saturated ester **7** in comparison to the non-silylated analogue **8** which would result from in cage attack, particularly at the beginning of the reaction when the concentration of **2** is larger. The second is the complete trapping of the *tert*-butyl radical by 0.1 M benzylidenemalonodinitrile (the alternative hypothesis that this involves quenching of excited **2** is incompatible with the low observed fluorescence quenching, see Table 1). Formation of the final products (**7**–**9**) involves hydrogen abstraction, but we have no evidence from the isolated products of which is the hydrogen source.

It is useful to note that the observed fragmentation is not a photochemical reaction characteristic of the silyloxy moiety *per se*, as shown by the photostability of **5**. Furthermore, this is not a reaction of the radical cation. Indeed, benzylidenemalonodinitrile is known to be alkylated when irradiated in the presence of benzyl- or allyl-trimethylsilane,[19] a reaction presumed to involve the corresponding radical cations. However, this reaction occurs at a reasonable rate only when a photosensitizer such as phenanthrene (Phen) is added. Under those conditions, the substrate radical cation is generated through secondary electron transfer to the initially formed, and quite persistent, Phen radical cation (see Scheme 3). This fact is deemed to be essential for the success of the reaction, since back electron transfer is less efficient than when a caged radical ion pair is formed primarily. In the present case, a Phen sensitized alkylation is indeed observed using the phenyl silyl ether **5**. Such a reaction is sluggish, due to the fact that the radical cation is here more stabilized than those of benzyl or allyl silanes (see above)[19] and the positive charge is localized on the phenoxy moiety. As a result, C–Si bond cleavage is much slower. Likewise, a small part of product **7** formed by irradiation of **2** in the presence of the phenoxy silyl ether **5** arises from intermolecular electron transfer and cleavage of $\mathbf{5}^{\bullet+}$. However, this path has a limited significance (compare the small difference in product distribution between entries 1 and 6 in Table 2) due to the inefficient quenching of excited **2**. On the contrary, the above dis-



Scheme 3

cussed photoinduced fragmentation of **2** does not require the presence of Phen (compare entries 2 and 4), and results from intramolecular, not intermolecular charge transfer.

The excited state of diester **3** can be described similarly to that of dinitrile **2**, but with a lesser degree of charge transfer, as shown by the blue shift of the fluorescence with respect to **2** and by the lower Stokes shift. Apparently, this is not sufficient to make photoinduced cleavage of the C–Si bond sufficiently fast to compete with physical decay.

A completely different situation is that encountered with 2-silyloxy derivatives such as **1**. One can draw zwitterionic mesomeric formulae for these compounds, and these are important in the excited state. Indeed, the spectrum undergoes a more fundamental transformation than in the case of isomeric **2**. A well separated and intensive ICT band is observed, and is red-shifted by over 5000 cm^{-1} with respect to the $\pi\pi^*$ band of benzylidenemalonodinitrile. In contrast to **2**, **1** shows no photochemical decomposition and very little fluorescence. This can be reasonably explained, since the lifetime of such ICT excited state is expected to be shortened by fast internal conversion (intramolecular back electron transfer), and furthermore the stabilization of the singlet excited state of **1** with respect to **2**^{1*} disfavours fragmentation.

In conclusion, this work shows that when excitation of conjugated molecules possessing both π-electron donating and accepting moieties leads to a certain degree of charge transfer, a fragmentation process typical of radical ions occurs at a rate competitive with physical deactivation. This might help us to devise new applications, *e.g.* for photochemical labelling in biology or photoinitiation in polymer science. This is not the case for the 'true' ICT states (*i.e.* those for which zwitterionic mesomers can be drawn), where the excited state is too short lived for a fragmentation to take place, as shown here by the difference between *ortho* and *meta* disubstituted benzylidenemalonodinitriles.

Experimental

Materials

The required 2-hydroxy- and 3-hydroxy-benzylidenemalonodinitirile and diethyl malonate[27–29] were prepared by Knoevenagel condensation (**CAUTION:** the malonodinitrile derivatives are strong sternutator and irritant agents). *J* values in Hz.

2-(2-*tert*-Butyldimethylsilyloxyphenyl)methylidenemalonodinitrile (1). A mixture of 2-(2-hydroxyphenyl)methylidenemalonodinitrile (1 g, 5.9 mmol), *tert*-butyldimethylsilyl chloride (1.08 g, 7.1 mmol), triethylamine (0.72 g, 1 mmol) and 4-dimethylaminopyridine (72 mg, 0.6 mmol)[30] in dichloromethane (50 ml) was stirred for 4 h at room temp. under nitrogen. The mixture was poured on a silica gel column and eluted with cyclohexane–ethyl acetate mixture (9:1). Evaporation of the yellow solution obtained gave a solid, 0.83 g (50% yield). Similarly obtained were the 3-silyloxy isomer (**2**, 75% yield) and the 3-silyloxy diethyl ester **3** (70% yield).

1, light-yellow crystals, mp 138–141 °C. Found: C, 67.5; H, 7.1; N, 9.7. Calc. for $C_{16}H_{20}N_2OSi$: C, 67.57; H, 7.09; N, 9.85%. $\delta_H(CDCl_3)$ 0.3 (s, 6H), 1.0 (s, 9H), 6.9 (d, *J*, 1H), 7.1 (dt, *J* 2, 8, 1H), 7.45 (dt, *J* 2, 8, 1H), 8.2 (dd, *J* 2, 8, 1H), 8.22 (s, 1H).

2, colourless crystals, mp 45.5–46 °C. Found: C, 67.4; H, 7.1; N, 9.7. Calc. for $C_{16}H_{20}N_2OSi$: C, 67.57; H, 7.09; N, 9.85%. $\delta_H(CDCl_3)$ 0.25 (s, 6H), 1.0 (s, 9H), 7.1 (dt, *J* 2, 8, 1H), 7.4 (m, 3H), 7.7 (s, 1H).

3, oil. Found: C, 63.6; H, 8.1. Calc. for $C_{20}H_{30}O_5Si$: C, 63.46; H, 7.99%. $\delta_H(CDCl_3)$ 1.0 (s, 9H), 1.32 (t, *J* 8, 3H), 1.35 (t, *J* 8, 3H), 4.30 (q, *J* 8, 2H), 4.35 (q, *J* 8, 2H), 6.85 (dd, *J* 2, 8, 1H), 6.95 (d, *J* 2, 1H), 7.05 (d, *J* 8, 1H), 7.22 (t, *J* 8, 1H), 7.55 (s, 1H).

Photochemical reactions

A solution of dinitrile **2** (350 mg) in acetonitrile (90 ml, 1.37 × 10^{-2} M) was subdivided in five 1 cm i.d. quartz tubes. These were purged with nitrogen for 20 min, stoppered with a serum cap and irradiated by means of six 15 W phosphor-coated lamps (centre of emission 320 nm) for 15 h. The solvent was rotary evaporated and the residue was chromatographed on silica gel eluting with cyclohexane–ethyl acetate mixtures (9–1 to 1–1) to give 17 mg (5%) of the starting material and products **6** (29 mg, 14%), **7** (223 mg, 53%), **8** (64 mg, 23%). Compound **6** was identical to the phenol used for the synthesis of **2**.

3-(3-*tert*-Butyldimethylsilyloxyphenyl)-2-cyano-4,4-dimethylpentanonitrile (**7**), oil. Found: C, 70.2; H, 8.9; N, 8.0. Calc. for $C_{20}H_{30}N_2OSi$: C, 70.13; H, 8.83; N, 8.18%. $\delta_H(CDCl_3)$ 0.2 (s, 6H), 1.0 (s, 9H), 1.1 (s, 9H), 2.95 (d, *J* 6, 1H), 4.2 (d, *J* 6, 1H), 6.85 (dt, *J* 1, 8, 1H), 6.9 (d, *J* 1, 1H), 7.0 (dt, *J* 1, 8, 1H), 7.25 (dt, *J* 1, 8, 1H). δ_C −4.5 (Me), 18.1, 24.9 (CH), 25.6, 28.4, 34.8, 56.4 (CH), 113.0 (CN), 113.1 (CN), 120.4 (CH), 121.0 (CH), 122.3 (CH), 129.6 (CH), 137.5, 159.9.

3-(3-Hydroxyphenyl)-2-cyano-4,4-dimethylpentanonitrile (**8**), oil. Found: C, 73.5; H, 7.1; N, 12.0. Calc. $C_{14}H_{16}N_2O$: C, 73.65; H, 7.06; N, 12.27%. $\delta_H(CDCl_3)$ 1.1 (s, 9H), 2.98 (d, *J* 6, 1H), 4.2 (d, *J* 6, 1H), 6.8–6.9 (m, 2H), 6.95 (d, *J* 8, 1H), 7.25 (t, *J* 8, 1H).

Under the conditions of Table 1, the following products were analogously obtained, in addition to the previously reported saturated dinitrile **9**.[31]

3,4-Bis(3-*tert*-butyldimethylsilyloxyphenyl)cyclobutane-1,1,2,2-tetracarbonitrile (**10**). Colourless crystals, mp 103–104 °C. Found: C, 67.6; H, 7.1; N, 9.8. Calc. for $C_{32}H_{40}N_4O_2Si_2$: C, 67.57; H, 7.09; N, 9.85%. $\delta_H(CDCl_3)$ 0.0 (s, 3H), 0.28 (s, 3H), 1.0 (s, 9H), 4.85 (s, 1H), 7.0–7.05 (m, 2H), 7.1 (d, *J* 8, 1H), 7.45 (t, *J* 8, 3H). $\delta_C(CDCl_3)$ −4.6, −0.1, 18.1, 25.5 (Bu^t), 36.3, 54.5 (CH), 111.6, 119.2 (CH), 120.3 (CH), 123.0 (CH), 129.6, 131.0 (CH), 156.8. The raw photolysate contained another cyclobutane dimer, as judged from the presence of a second singlet at δ 4.7 (ratio *ca.* 1 to 2) in the ^{1}H NMR and the doubling of several ^{13}C signals.

Acknowledgements

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