

Photoinduced Novel Silylation of CF₃-substituted Benzenes with Disilane and Trisilane

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Irradiation of CF₃-substituted benzene in the presence of hexamethyldisilane and octamethyltrisilane causes two types of photosilylation, namely one at a benzylic position to give the corresponding benzylic silanes, and the other at aromatic ring to afford the corresponding phenylsilanes.

Photoinduced electron-transfer reactions of aromatic nitriles as strong acceptors have been attracting much interest from the mechanistic and synthetic viewpoints.¹ Recently, we have demonstrated that organometallic compounds serve as good σ -donors and undergo alkylation and silylation of aromatic

nitriles *via* photoinduced electron transfer.² As part of our continuing research on the electron-transfer chemistry of organometallic compounds, we investigated the photoreaction of organosilicon catenates with CF₃-substituted benzenes (**1–3**), which are relatively weak acceptors and have so far

been overlooked for electron donor-acceptor reactions.³ We report here the novel photosilylation of CF₃-substituted benzenes using disilane and trisilane.

A cyclohexane solution of hexamethyldisilane (**4**; 0.1 mol dm⁻³) and CF₃-substituted benzenes (**1–3**, 0.1 mol dm⁻³) was irradiated with a mercury-arc lamp under an argon atmosphere.[†] The products were separated by preparative GLC and trimethylsilylfluoride was detected by GC-MS. All new compounds gave satisfactory spectral data and the yields were determined by GLC. The results are summarized in Table 1.

Cophotolysis of **1** and **2** with the disilane resulted in silylation at benzylic position and aromatic ring as shown in

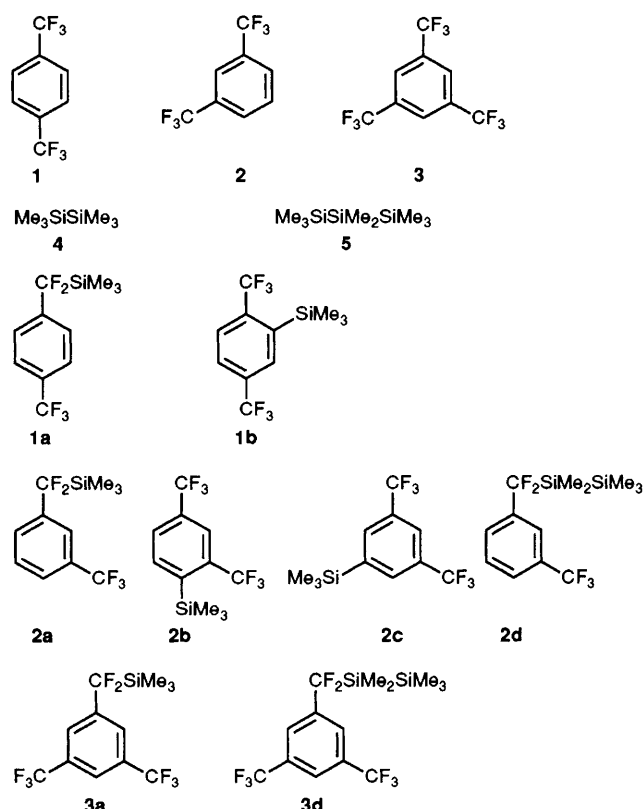


Table 1 Photosilylation of CF₃-substituted benzenes **1–3** with disilane **4** and trisilane **5**

CF ₃ -substituted benzene	Me(Me ₂ Si) _n Me	Products [yield (%)] ^a
1	4 ^b	1a (17), 1b (5)
2	4 ^b	2a (9), 2b (8), 2c (19)
3	4 ^b	3a (11)
1	5 ^b	1a (2), 1b (3)
2	5 ^b	2a (1), 2b (2), 2c (3), 2d (3)
3	5 ^b	3d (13)
1	5 ^c	1a (7), 1b (9)
2	5 ^c	2a (4), 2b (4), 2c (–), 2d (10)
3	5 ^c	3d (19)
1	4 ^d	1a (49), 1b (20)
2	4 ^d	2a (26), 2b (13), 2c (46)
3	4 ^d	3a (14)

^a In general cases, along with the products above considerable amounts of unidentifiable polymers were formed. ^b Irradiated with a 125 W low-pressure Hg-arc lamp. ^c Irradiated with a 500 W medium-pressure Hg-arc lamp. ^d Irradiated with a 500 W medium-pressure Hg-arc lamp through a Pyrex filter in the presence of phenanthrene.

[†] Compounds **1** and **2** were irradiated with a 125 W low-pressure Hg-arc lamp and **3** was irradiated with a 500 W medium-pressure Hg-arc lamp through a Pyrex filter.

Table 1. In the case of *m*-isomer **2**, the product silylated at the 2-position was not detected in the photolysate. This is probably due to steric repulsion against introduction of the silyl group to the 2-position. Meanwhile, when **3** was photolysed in the presence of **4**, the silyl group was introduced to CF₃ group exclusively and none of the ring-silylated product was detected in the photolysate as expected from the result of **2**. Thus, the silylation occurs in two different ways, and is dependent on the substitution pattern of the CF₃-substituted benzenes employed. When octamethyltrisilane **5** was used instead of **4**, a very similar silylation occurred except that some of disilanyl-substituted products (**2d** and **3d**) were obtained. The formation of trimethylsilyl- and pentamethyltrisilanyl-fluoride was confirmed by GC-MS analysis.

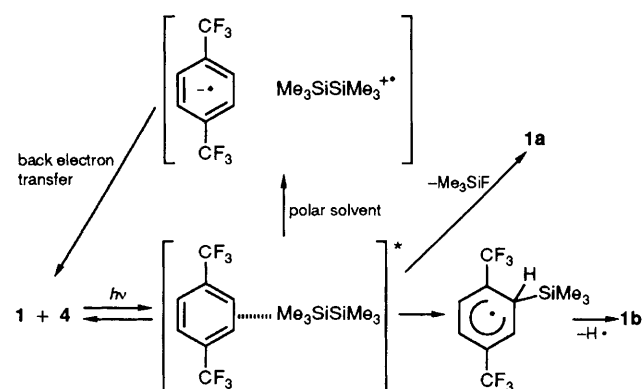
In the absence of **1–3**, disilane **4** and trisilane **5** are stable under the photolytic conditions. No charge-transfer interaction between **1–3** and **4** or **5** was detected in the UV-VIS region. The fluorescence of **1–3** was quenched by **4–5** at nearly diffusion-controlled rates in cyclohexane (Table 2). The reaction could not be quenched in the presence of buta-1,3-diene, which has relatively low triplet excited energy.⁴ Negative free energy changes (ΔG) were obtained for the electron transfer between **3** and **4–5** by the Rehm-Weller equation,⁵ but those for **1** and **2** were positive (Table 2). Furthermore, the photosilylation did not take place in acetonitrile, which usually accelerates electron-transfer reactions. From these results, we tentatively propose the mechanism shown in Scheme 1, which represents the case of **1** and **4**, and involves exciplexes as key intermediates although the exciplex emission was not observed. Mattay *et al.* observed a similar solvent effect in the photoreaction of trifluoromethylbenzene with olefins and suggested formation of an exciplex at the initial stage.³ The formation of ring-silylated products **1b**, **2b** and **2c** implies intermediacy of silyl radicals, which are known to undergo aromatic substitution readily.⁶

The yields of the photoproducts were not satisfactory in general while a significant amount of complex polymeric materials was formed as byproduct. Interestingly, when the reaction was carried out in the presence of 10 mol% of phenanthrene with irradiation using a medium-pressure Hg-

Table 2 Calculated ΔG values for the one-electron-transfer process between donor-acceptor and rate constants (k_q) for the fluorescence quenching in cyclohexane

Acceptor	Donor	$\Delta G/\text{kcal mol}^{-1a}$	$k_q/10^{-9} \text{ dm}^3 \text{ mol}^{-1}$
1	4	+9.5	5.99
2	4	+9.9	1.52
3	4	-1.6	3.45
1	5	+6.7	8.47
2	5	+9.9	3.81
3	5	-4.4	5.18

^a 1 cal = 4.184 J.



Scheme 1

arc lamp through a Pyrex filter, the yields of products increased substantially (see, Table 1, footnote *d*). In the absence of phenanthrene the silylation did not take place at all under these conditions and the starting materials were recovered quantitatively. Since the photoproducts are kinds of benzyl or phenyl silanes, these results suggest a potential route to silyl fluorocompounds as useful fluorinated group transfer reagents.^{7,8} Further detailed studies of the reaction mechanism are in progress.

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