Photochemistry of [Tris(trimethylsilyl)methyl]benzene

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Irradiation of [tris(trimethylsilyl)methyl]benzene (trisylbenzene) (**1**) gave mainly [bis(trimethylsilyl)methyl]-*p*-trimethylsilylbenzene (**2**) and [bis(trimethylsilyl)methyl]benzene (**3**); a free radical mechanism is proposed.

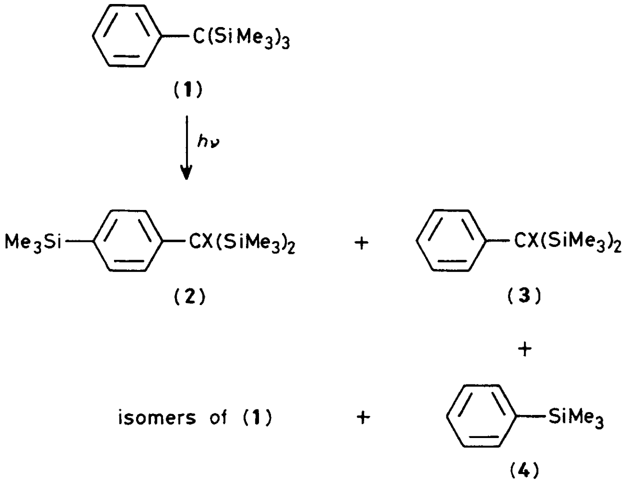
Recently considerable attention has been focused on the chemistry of sterically crowded organosilicon compounds such as tris(trimethylsilyl)methyl (trisyl) derivatives.[1] However, no photochemical reaction of trisyl derivatives, except for trisyl iodides[2] and ditrisyl mercury,[3] has been reported so far. In connection with our current interests in the photochemistry of organosilicon compounds,[4] especially of benzylsilanes,[5] we became interested in the photochemistry of trisylbenzene (**1**).

Although benzyltrimethylsilane[6] and [bis(trimethylsilyl)-methyl]benzene remain almost intact on irradiation,† irradiation (254 nm) of (**1**) in benzene for 0.5 h gave products (55% conversion) consisting of [bis(trimethylsilyl)methyl]-*p*-trimethylsilylbenzene (**2a**) (64%), [bis(trimethylsilyl)-methyl]benzene (**3a**) (5%), phenyltrimethylsilane (**4**) (trace), and a mixture of at least five isomers of (**1**) (*ca.* 30%). The latter were detected by g.c.–mass spectroscopy but structures were not determined.

Addition of a few drops of DCl under the same conditions increased both the % conversion of the reaction (72%) and the yield of (**2**) (69%). Compound (**3**) (3%) and isomers of (**1**) (*ca.* 20%) were also formed. All the deuterium incorporated in (**2**) occurs at the benzylic position [(**2b**)/(**2a**) = 1.3]. The deuterium content of (**3**) was 37%, but the position of D was not identified. The deuterium content of three isomers of (**1**) was also examined. One isomer contained 56% deuterium but the other two isomers contained none at all.

Similar irradiation of (**1**) in benzene–[$^2H_1$]methanol (1 : 1 v/v ratio) resulted in the formation of only (**3**) (82%) and *ca.* 10% of isomers of (**1**). No trace of (**2**) was detected. All the deuterium in (**3**) was located in the benzylic position [(**3b**)/(**3a**) = 19].

The reaction of (**1**) is thus best explained as shown in Scheme 1. The importance of σπ conjugation in trisylbenzene



a; X = H
b; X = D

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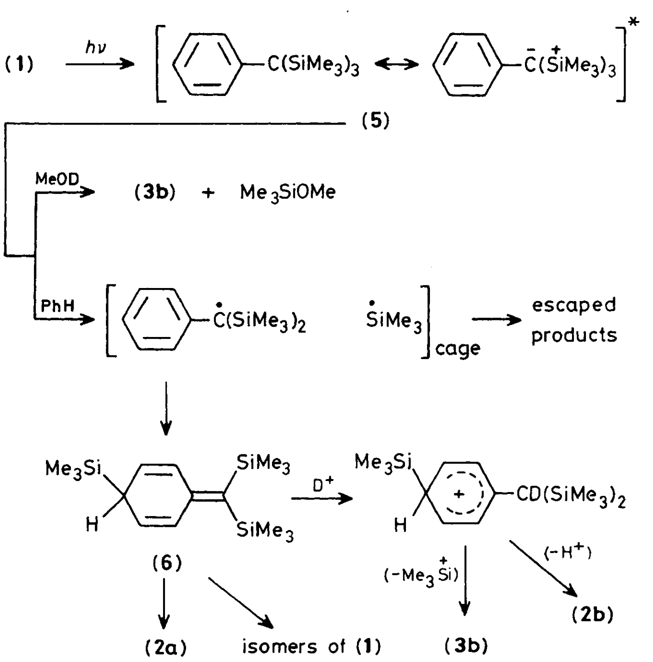
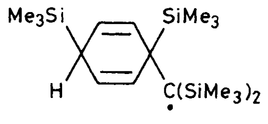
† Irradiation of benzyltrimethylsilane yielded, in our experiments, a trace amount of *o*-trimethylsilyltoluene.



Scheme 1

derivatives[7] as well as in the parent benzylsilanes[8] to determine the electronic structures has been demonstrated previously. The charge-separated structure, in which positive and negative charges are located on silicon and benzylic carbon atoms, should be an important contributor to the excited state (or species responsible for the reaction) of (**1**), *i.e.* (**5**). Direct solvolysis of (**5**) by methanol then leads to the formation of (**3**). However, in non-polar media, (**5**) collapses to a pair of phenylbis(trimethylsilyl)methyl and trimethylsilyl radicals which then gives a substitution product (**6**) followed by rearrangement to (**2a**). Addition of DCl afforded (**2b**). The escaped trimethylsilyl and phenylbis(trimethylsilyl)methyl radicals gave phenyltrimethylsilane (**4**) and (**3a**).

Irradiation of a benzene solution of (**1**) in an e.s.r. cavity revealed the formation of a persistent radical: $a(^1H) = 0.028$ mT (18H), 0.084 mT (2H), $a(^{13}C) = 0.48$ mT, $a(^{29}Si) = 1.31$ mT (2Si), 2.29 mT (1Si), $g = 2.0022$. We tentatively assign the structure (A) to the radical formed by the addition of the trimethylsilyl radical to the intermediate (**6**).



(A)

Apparently, the driving force of the present photochemical reaction is the sterically crowded structure of (**1**). The back reaction of the excited species (**5**) or the radical pair to (**1**), which is seemingly the major pathway in the photochemical reaction of benzyltrimethylsilane, should therefore be retarded. In accord with this, we have observed a very low quantum yield of the fluorescence of (**1**) (0.012) compared with that of benzyltrimethylsilane (0.138).

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