Novel Silylation of Aromatic Nitriles *via* Photo-induced Electron Transfer†

Soichiro Kyushin, Yasushi Ehara, Yasuhiro Nakadaira, and Mamoru Ohashi*

Department of Applied Physics and Chemistry, The University of Electro-Communications, Chofu, Tokyo 182, Japan

Photo-induced electron transfer reactions of hexamethyldisilane and aromatic nitriles have been examined; hexamethyldisilane acts as an effective σ-donor, and undergoes novel photochemical silylation of aromatic nitriles.

Photo-induced electron transfer reactions of good electron accepting aromatic nitriles have been studied extensively,[1] and various types of electron donors have been employed: *i.e.*, π-donors such as aromatic compounds,[2] ethylene derivatives,[3] and allyl and benzyl metalloidal compounds;[4] n-donors such as amines[5] and ethers;[6] σ-donors such as strained hydrocarbons.[7] Recently, peralkylpolysilanes have been proved to act as good σ-electron donors to form charge-transfer complexes with tetracyanoethylene (TCNE)[8] and undergo photo-induced electron transfer reactions with 9,10-dicyanoanthracene.[9] We describe here photo-induced electron transfer reactions and novel photochemical silylation of aromatic nitriles with hexamethyldisilane.

Acetonitrile solutions of hexamethyldisilane (0.5 M) and aromatic nitriles [(**1**)—(**6**), 0.1 M] were irradiated with a mercury lamp under an argon atmosphere.‡ The products were separated by t.l.c. on silica gel and the yields were determined by g.l.c. The results are summarized in Scheme 1.

On irradiation, (**1**) and hexamethyldisilane afforded *o*- and *p*-trimethylsilylbenzonitriles (**7**) and (**8**) selectively as silylated products, and the corresponding *m*-isomer was not detected in the photolysate. This is in contrast with the selectivity usually observed in the electrophilic aromatic substitution of (**1**). In the case of dicyanobenzenes (**2**)—(**4**), the position of the introduced trimethylsilyl group is highly dependent on the substitution pattern of the aromatic ring. Thus in the *o*- and *p*-isomers (**2**) and (**4**), silylation occurred exclusively on the ring carbon bearing the cyano substituent and expelled the cyano group to yield (**7**) and (**8**), respectively, together with

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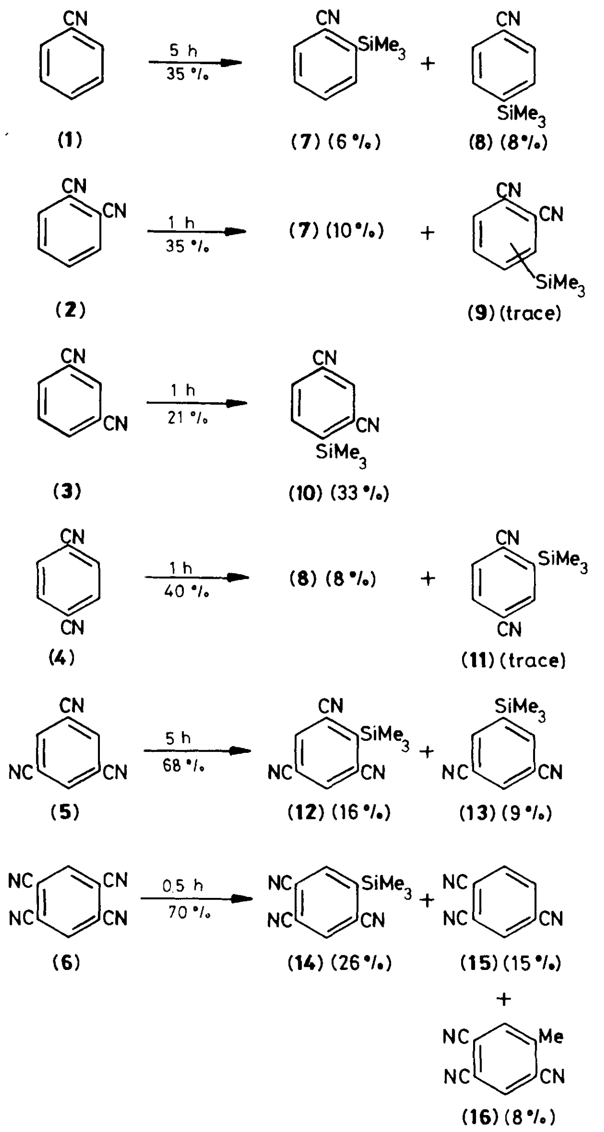
† Presented in part at the 56th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1—4, 1988; Abstr. II, p. 1448.

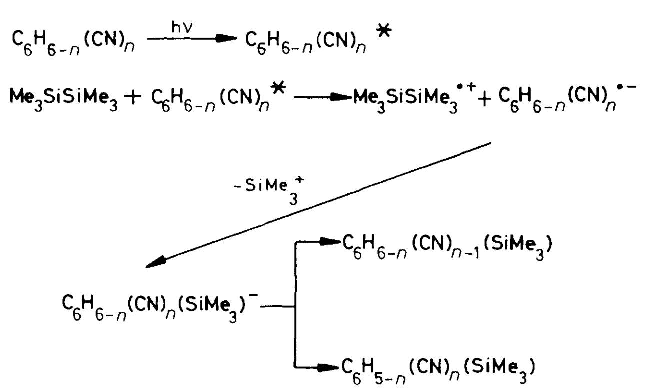
‡ Compounds (**1**)—(**5**) were irradiated with a 100 W low-pressure mercury lamp. Compound (**6**) was irradiated with a 500 W medium-pressure mercury lamp through a Pyrex filter.



Scheme 1. Photochemical silylation of the aromatic nitriles (1)—(6) with hexamethyldisilane. % Conversions after the reaction times noted are given under the arrows.

trace amounts of (**9**) and (**11**). In contrast, in the case of the *m*-isomer (**3**), the silyl group was introduced to the 4-position only to give (**10**). Tricyanobenzene (**5**) gave both types of products (**12**) and (**13**), but (**12**) was preferred as in the cases of (**1**) and (**3**), while in tetracyanobenzene (**6**), one of the cyano groups was expelled exclusively to give a silylated product (**14**) similarly to the cases of (**2**) and (**4**). Minor amounts of (**15**) and a methylated product (**16**) were also formed, unexpectedly (**16**) apparently being formed by the reaction of (**6**) and acetonitrile.[10] These results indicate that the silylation occurs in two different ways, and is highly dependent on the substitution pattern of the starting aromatic nitriles.

Although a charge-transfer interaction between aromatic nitriles and hexamethyldisilane was not detected in the u.v.-visible region, the fluorescence of (**2**)—(**6**) was quenched by hexamethyldisilane at nearly diffusion controlled rates in acetonitrile. Coupled with a negative free energy change calculated for the electron transfer from hexamethyldisilane to (**2**)—(**6**),[11] these results are reasonably accounted for by the electron transfer from hexamethyldisilane to the excited singlet state of the aromatic nitrile to form a radical-ion pair.



Scheme 2

It is interesting that the position of silylation is in accord with that having maximum spin density in the benzene ring of the cyanobenzene radical anions, which may be simply calculated by Hückel and McLachlan M.O. methods and estimated by e.s.r. spectroscopy.[12] For example, the spin density is largest on C(1) in (**2**)$^{\cdot-}$, C(4) in (**3**)$^{\cdot-}$, and C(1) in (**4**)$^{\cdot-}$. These are just the positions of silylation with the disilane under the photo-induced electron transfer conditions (Scheme 1). This finding implies that the radical part of the hexamethyldisilane radical cation attacks the cyanobenzene anion radical followed by either elimination of a cyanide ion or back electron transfer to the cation counterpart and elimination of hydrogen (Scheme 2).

We thank Professor Noboru Mataga of Osaka University and Professor Katsumi Tokumaru of the University of Tsukuba for measurement of lifetimes of fluorescence of aromatic nitriles. The work was partially supported by a Grant-in-Aid for Special Project Research No. 61123005 and No. 63104003 from the Ministry of Education, Science and Culture.

Received, 19th September 1988; Com. 8/03549K

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