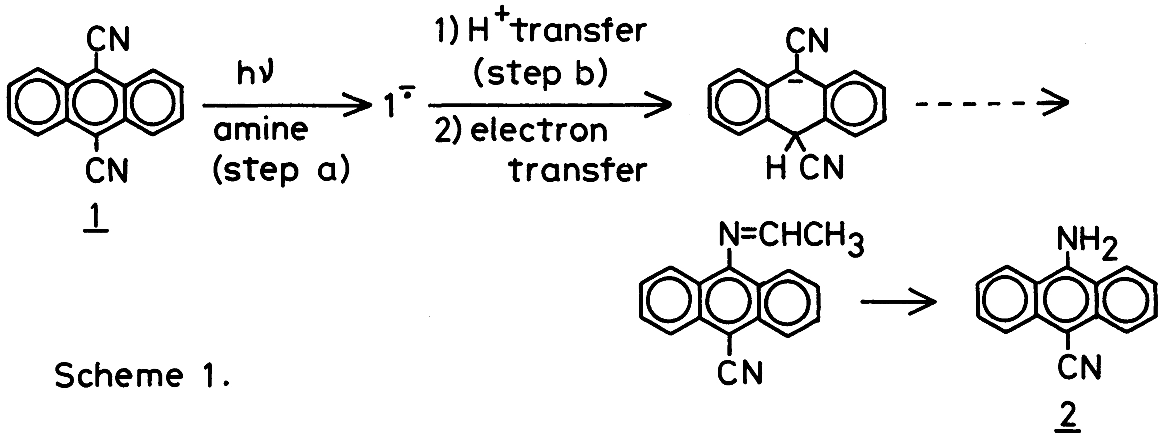
CHEMISTRY LETTERS, pp. 361-364, 1986.

PHOTOCHEMICAL AMINATION OF TETRACYANOBENZENE WITH ACETONITRILE IN THE PRESENCE OF ALIPHATIC AMINE

Shuzo YAMADA, Yoshiki NAKAGAWA, Oserojoin WATABIKI,
Shin-ichi SUZUKI, and Mamoru OHASHI*
Department of Materials Science, The University of Electro-
Communications, Chofu, Tokyo 182

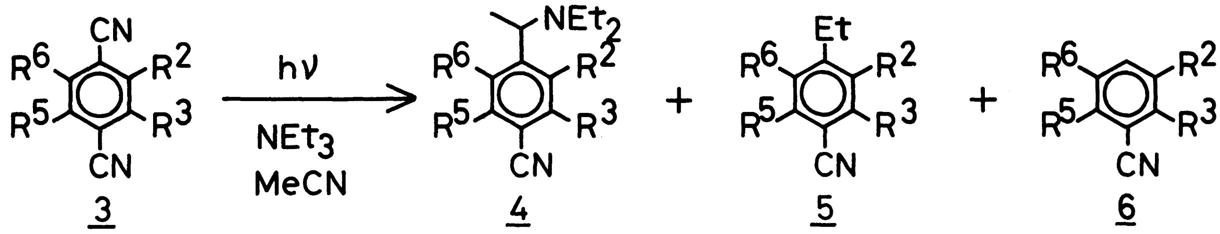
Irradiation of dicyanoxylenes and dicyanodurene in acetonitrile in the presence of triethylamine gave mainly substitution and reduction products respectively, whereas a photochemical reaction of 1,2,4,5-tetracyanobenzene in the presence of N-methylpyrrolidine or nicotine gave tricyanoaniline, an amination product, as well as substitution products.

The photochemical reactions of aromatic nitriles with aliphatic amines may take several routes such as the Birch reduction, addition or substitution at the N or α-C position of the starting amines[1-3] to give various products. In 1979 we reported, however, that irradiation of 9,10-dicyanoanthracene(1) in wet (6%) acetonitrile in the presence of a primary, secondary, or tertiary amine yielded not the expected 1:1 adduct of the amine to 1, but 9-amino-10-cyanoanthracene(2), a reaction product between 1 and acetonitrile.[4] We have proposed tentatively



Scheme 1.

the mechanism shown in Scheme 1 for this unique reaction. In order to clarify the factors discriminating the reaction route in favor of the amination, and to find other examples of amination with acetonitrile, we examined photochemical reactions of several 1,4-dicyanobenzene derivatives(3a-d). In a typical run 2,5-dimethyl-1,4-dicyanobenzene(3b)(200 mg) in acetonitrile-triethylamine(9:1, 85 ml) was irradiated with a 6 W low pressure mercury arc lamp through quartz for 6 h under nitrogen. The product mixture was separated by column chromatography to give 4b, 187 mg (67%), oil, ^{1}H-NMR(CCl$_4$) δ 7.32(1H, br s) 7.24(1H, br s) 3.89 (1H, q, J=7 Hz) 2.47(3H, s) 2.34(3H, s) 2.1-2.7(4H, m) 1.21(3H, d, J=7 Hz) 0.92 (6H, t, J=7 Hz); MS(20 eV) m/z 230(M$^+$,9) 215(82) 158(61) 100(100) and 5b, 29 mg (13%), oil, ^{1}H-NMR(CCl$_4$) δ 7.20(1H, s) 7.00(1H, s) 2.49(2H, q, J=7 Hz) 2.40(3H, s) 2.23(3H, s) 1.19(3H, t, J=7 Hz); MS(20 eV), m/z 159(M$^+$, 40) 144(100) 130(9). The dicyanoxylenes(3b and 3c) gave mainly substitution products, while dicyanodurene(3d) gave mainly a reduction product (6). Scheme 2 and Table 1 summarize the results.



Scheme 2.

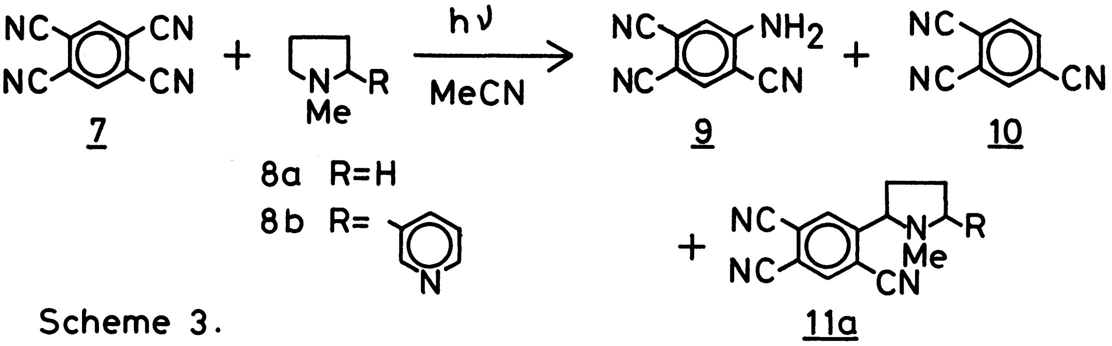
Table 1. Yield(%) of the Products (4-6) by the Irradiation of Compounds (3a-d)

Substrate	R^2	R^3	R^5	R^6	4	5	6
3a	H	H	H	H	18	56	-
3b	Me	H	Me	H	67	13	-
3c	H	Me	Me	H	45	28	-
3d	Me	Me	Me	Me	-	-	38

It became clear from these results that steric factors alter the reaction route from substitution to reduction but not to amination, and an electronic factor as well as the steric factor seemed to play an important role in the amination. We also found that since neither 1,4-diazabicyclo[2.2.2]octane nor tribenzylamine was effective for the amination of 1 in spite of the good electron donor character, not only the initial electron-transfer (step a in Scheme 1) but also the successive proton-transer (step a-b) must be essential.

On the basis of those facts we concluded at this stage that requirements for amination might be; i) either the amine or the aromatic nitrile has bulky sustituents, ii) proton-transfer between the radical cation-radical anion pair occurs easily, and iii) the reduction potential of aromatic nitrile is substantially high.

Considering those requirements we tried the photochemical reaction of 1,2,4,5-tetracyanobenzene(7) in wet acetonitrile in the presence of N-methylpyrrolidine (8a) as the most promising candidate of amination reaction. We designed this particular reaction system, because reduction potential of 7 is higher than those of 3a-d, and 8a may work as an electron donor with steric hindrance.5) In a typical case 7 (259 mg) was irradiated in wet acetonitrile(70 ml) in the presence of N-methylpyrrolidine(8a) (10 ml) with a 100 W medium pressure mercury arc lamp through Pyrex filter for 20 h under nitrogen. The expected amination product, 2,4,5-tricyanoaniline(9)6) was obtained after preparative TLC(silica) separation in 3% yield together with the reduction (10) and substitution (11) products. The yield of 9 was low in this case but replacement of nicotine(8b) for 8a in a similar irradiation of 7 increased the production of 9 up to 12% yield.



Scheme 3.

To clarify the origin of the nitrogen in the amino group of 9, we carried out a similar photochemical reaction of 7 in 90% aqueous acetonitrile-^{15}N(96.9 atom percent) in the presence of N-methylpyrrolidine. The mass spectrum of the product showed that 37% of the product was ^{15}N-incorporated. This result is in sharp contrast with the case of 1 in which almost all of the amino group of 2 was ^{15}N-incorporated. In the case of 7-pyrrolidine(8) system the cyano group of unexcited 7 present in the neighborhood of the excited 7 may probably compete with the cyano group of acetonitrile as the substitution reagent and non-labelled nitrogen of 7 may be incorporated in the amination product(9).

Although the origin of the amino nitrogen of 9 is not yet fully elucidated, we report here that the second example of photo-induced amination with acetonitrile has been successfully designed based on the logical extension of photo-induced electron-transfer reactions of polycyanoaromatics with sterically hindered aliphatic amines.

This work was supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

References

1) A. Gilbert, S. Krestonosick, and D. L. Westover, J. Chem. Soc., Perkin Trans. 1, 1981, 295.
2) M. Ohashi, K. Miyake, and K. Tsujimoto, Bull. Chem. Soc. Jpn., 53, 1683(1980).
3) F. D. Lewis, B. E. Zebrowski, and P. E. Correa, J. Am. Chem. Soc., 106, 187 and 194(1984); F. D. Lewis, Acc. Chem. Soc., 12, 152(1979).
4) M. Ohashi, H. Kudo, and S. Yamada, J. Am. Chem. Soc., 101, 2201(1979).
5) Irradiation of 7 in acetonitrile in the presence of triethylamine gave various products, but 9 was not detected in the product mixture.
6) Mp 232 °C(dec.), ^{1}H-NMR(CD$_3$CN) δ 7.88(1H, s) 7.20(1H, s) 5.5-6.2(2H, br s); IR(Nujol) 3430, 3330, 3240, 2240 cm^{-1}; MS(20 eV) m/z 168(M^{+}-HCN, 36).

(Received December 24, 1985)