Preparation of 1,4-Dicyanobenzene Derivatives and the Substituent Effect of the Sensitizers on Photoinduced Electron-Transfer Reactions

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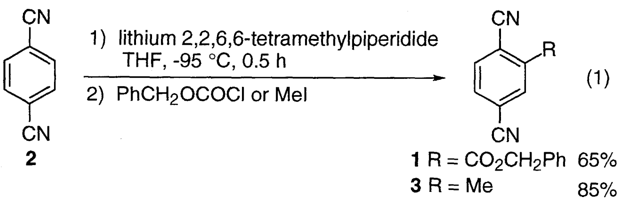
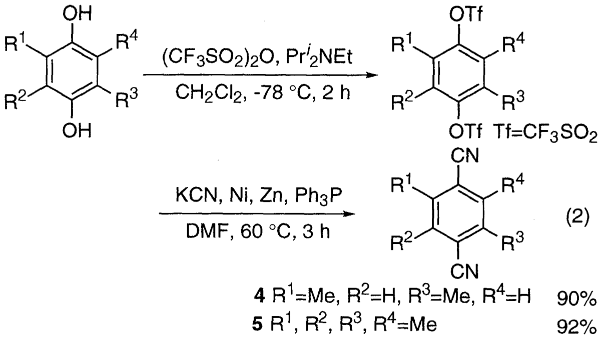
Substituted 1,4-dicyanobenzenes are prepared as electron-accepting photosensitizers. The efficiency of some photosensitized reactions is influenced remarkably by the substituent(s) of 1,4-dicyanobenzene. By using mono or dimethylated dicyanobenzene, the reactions proceed more rapidly as compared with that by using 1,4-dicyanobenzene itself.

Photoinduced electron transfer reactions are potentially of great interest to synthetic organic chemists.[1~3] However, they proceed not so efficiently in the sence of synthetic reactions, generally affording low yield of products. We found that the efficiency of some photochemical reactions are remarkably influenced by the substituent(s) of a photosensitizer, 1,4-dicyanobenzene. We prepared some substituted 1,4-dicyanobenzenes, such as benzyl 2,5-dicyanobenzoic ester (**1**), 2-methyl-1,4-dicyanobenzene (**3**), 2,5-dimethyl-1,4-dicyanobenzene (**4**), and 2,3,5,6-tetramethyl-1,4-dicyanobenzene (**5**)[4] as follows.

2-Substituted 1,4-dicyanobenzene derivatives, benzyl 2,5-dicyanobenzoic ester (**1**) and 2-methyl-1,4-dicyanobenzene (**3**), were prepared by the reaction of 2-lithio derivative of 1,4-dicyanobenzene (**2**) with electrophiles. Though 2-lithio-1,4-dicyanobenzene is reported to be unstable even at -78 °C,[5] it was found that 1,4-dicyanobenzene was lithiated with lithium 2,2,6,6-tetramethylpiperidide at -95 °C in tetrahydrofuran and the lithiated dicyanobenzene was kept without a detectable amount of decomposition at least for 30 min. By treatment of the lithiated dicyanobenzene with benzyl chloroformate and methyl iodide, 2,5-dicyanobenzoate **1** and 2-methyldicyanobenzene **3** were obtained in good yield, respectively (eq. 1).



Usually, poly substituted 1,4-dicyanobenzenes have been prepared by the reaction of the corresponding poly substituted 1,4-diiodobenzenes with copper cyanide, however, the yield of the products is not so high.[4] Poly alkyl substituted dicyanobenzenes were found to be synthesized by cyanation of substituted *p*-hydroquinones. That is, 2,5-dimethyl and 2,3,5,6-tetramethyl-*p*-hydroquinones were converted to the corresponding bis-triflates by treatment with trifluoromethanesulfonic acid anhydride and diisopropylethylamine. The reaction of the resulting bis-triflates with potassium cyanide in the presence of catalytic amounts of nickel, zinc, and triphenylphosphine[6] gave 2,5-dimethyl-1,4-dicyanobenzene (**4**) and 2,3,5,6-tetramethyldicyanobenzene (**5**) in 90% and 85% yield, respectively (eq. 2).



By employing these singlet photosensitizers, electron tranfer bond cleavage reaction of 6,6-diphenyl-1,4-dioxaspiro-[4.5]decane (**6**) was examined (eq. 3).[1] The typical experimental procedure is as follows: A methanol-acetonitrile solution (1:3) of equimolar amounts of the spiroacetal **6** and a photosensitizer (0.03 M concentration) was irradiated for 20 h in a quartz tube using a high pressure mercury lamp.[7] The solvent was evaporated, and the reaction mixture was treated with 5% hydrogen chloride-methanol solution. The reaction was quenched by pH 7 buffer. After purification by thin-layer chromatography (silica gel, hexane : ethyl acetate = 95 : 5), a ring-opened product **7** were obtained and **6** was recovered as a acid-hydrolyzed 2,2-diphenylcyclohexanone **8**. The sensitizers **1**~**5** were recovered quantitatively. As shown in Table 1, the ester **7** was obtained in 95% yield by the use of the monomethyl dicyanobenzene **3**, while the yield was about 25% when the reaction was performed with the dicyanobenzoate **1** or the dicyanobenzene **2**. The use of the dimethy dicyanobenzene **4** further accelerated the reaction as compared with that using the monomethyl derivative **3**. Even in the shorter reaction time (3 h), the ester **7** was obtained in 65% yield, whereas the use of the monomethyl derivative **3** afforded the ester **7** in 43% yield. The bond cleavage reaction did not proceed by the use of the tetramethyl dicyanobenzene **5**, and **6** was recovered as the ketone **8**.

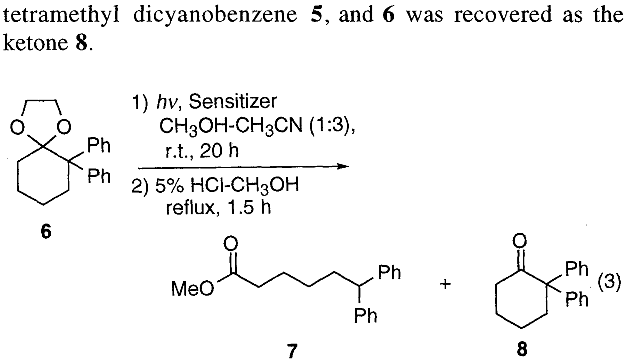
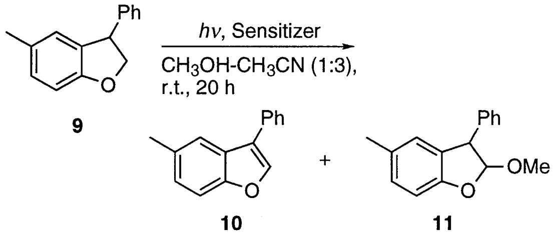


Table 1. The Photochemical Reaction of **6** Using Various Sensitizers

Sensitizer	Time / h	Yield / % **7**	**8**
1	20	26	73
2	20	25	75
3	20	95	0
3	3	43	55
4	3	65	34
5	3	0	95

This photoreaction proceeds through an electron transfer between the singlet exited state of sensitizer and the substrate **6**, giving the anion radical of the sensitizer and the cation radical of **6**.[1] Methyl-substituted dicyanobenzenes **3** and **4** promoted the reaction more efficiently than dicyanobenzene **2** itself. This remarkable substituent effect of sensitizers is explained presumably by considering the back electron transfer step between the cation radical of **6** and the anion radicals of sensitizers. Concerning the back electron transfer, the alkyl substituent effect of donors has been well studied by Gould[8]: That is, when the energy gap between an oxidation potential of a donor (D) and a reduction potential of an acceptor (A) is larger than 2 eV, a rate of the back electron transfer between $D^{+\bullet}$ and $A^{-\bullet}$ decreases more as the energy difference becomes larger.[8] The oxidation potential of the spiroacetal **6** was reported as 2.14 V(vs SCE).[1] The reduction potentials of 1,4-dicyanobenzene (**2**) and 2,3,5,6-tetramethyl-1,4-dicyanobenzene (**5**) are measured by Gassman to be -1.72 V(vs SCE) and -1.92 V(vs SCE), respectively.[9] Accordingly, it is supposed that the reduction potentials of dicyanobenzene derivatives becomes lower as increasing the number of the methyl substituent. Hence, the back electron transfer is more suppressed by employing the methylated dicyanobenzenes **3** and **4**.

As mentioned, in the reaction using the tetramethyl sensitizer **5**, the reaction did not occur at all. Probably, the exited state reduction potential of **5** is not high enough to oxidize the substrate **6**.

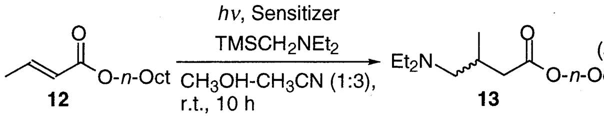


(4)

Sensitizer	Yield **10**	**11**
2	12 %	5 %
3	29 %	0 %
4	13 %	41 %

Since a remarkable substituent effect of sensitizers was observed, the photosensitized oxidation reaction of a dehydrobenzofuran **9** was examined with the dicyanobenzenes **2**, **3**, and **4**.[2] Total yield of the oxidized product **10** and its methanol adduct **11** was increased from 17% to 29% and 54%, respectively, when the reaction was performed with the dicyanobenzene **2** and the methylated 1,4-dicyanobenzene **3** and **4**.

The photosensitized aminomethylation reaction of octyl crotonate (**12**) was tried by applying the procedure of Mariano (eq. 5), where dicyanonaphthalene was employed as a sensitizer.[10] The starting material **12** was recovered by the use of the dicyanobenzene **2**, however, 2-methyldicyanobenzene **3** promoted the photosensitized aminomethylation. Though the yield of the product was low, the corresponding γ-amino butanoate **13** was obtained.



(5)

Sensitizer	Yield **13**
2	0 %
3	10 %

Thus, even with a small modification of photosensitizers, the efficiency of photosensitized electron transfer reactions could be improved to a great extent.

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References and Notes

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