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PHOTO- AND RADIATION-INDUCED ALCOHOLYSIS AND SUBSTITUTION OF p-DICYANOBENZENE IN 2-PROPANOL

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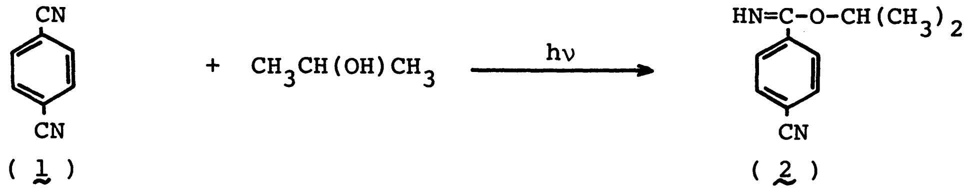
The irradiation of p-dicyanobenzene with 254 nm light in 2-propanol causes the alcoholysis of CN group to give isopropyl p-cyanobenzimidate. The UV-irradiation in the presence of acetone or γ-irradiation brings about the substitution of a cyano group by the hydroxyalkyl group derived from the alcohol. The substitution occurs via the electron transfer from hydroxyalkyl radicals or electrons followed by the attack of hydroxyalkyl radicals.

Photochemical reactions of aromatic and heteroaromatic carbonitriles have been extensively investigated. Their most characteristic photoreaction is the substitution of the cyano group.1-3) Most of these photoreactions are initiated by the photo-induced electron transfer in the CT-complexes formed in the ground state4) or by the electron transfer via an exciplex.5)

We report here that the direct photolysis of the p-dicyanobenzene — 2-propanol system brings about the alcoholysis of the cyano group rather than the substitution. Either the photolysis in the presence of acetone or γ-radiolysis of the system, however, brings about the substitution similar to those in the photoreaction of CT-complexes or of exciplexes via the electron transfer from hydroxyalkyl radicals or solvated electrons.

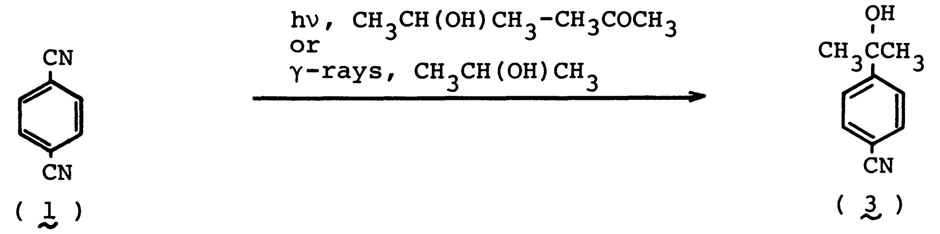
Deaerated 2-propanol solutions of p-dicyanobenzene(**1**)(0.01 mol dm^{-3}), containing additives if necessary, were irradiated with a mercury lamp (a low or a high pressure mercury lamp) or with Co-60 γ-rays. The products were separated by means of TLC or GLC and identified spectroscopically.6) Quantitative analyses were done by means of GLC (column, 2 m column of PEG 20M 5% on Celite; column temperature, 200 °C).

The results are summarized in Table 1 and 2. The 254 nm irradiation of **1** in 2-propanol in the absence of additives causes the alcoholysis of one cyano group to give isopropyl p-cyanobenzimidate(**2**).



Similar photo-induced solvolyses have been reported for o-acetylaminobenzonitrile[7)] and for N-cyanopiperidine.[8)] Compound **1** has no UV-absorption in the region of the emission of a high pressure mercury lamp. Because of this, the photo-reactivity of **1** in the irradiation with a high pressure mercury lamp is low.

The irradiation of **1** in 2-propanol in the presence of acetone brings about the substitution of one cyano group by a 1-hydroxy-1-methylethyl group. The same type of reaction occurs when **1** is irradiated in 2-propanol with Co-60 γ-rays.



The accordance of the photoreaction in the presence of acetone with the radiation-induced reaction suggests that the substitution of CN by 1-hydroxy-1-methylethyl group is not due to the triplet excited state of **1**, but due to 1-hydroxy-1-methylethyl radicals which are formed both in the photoreaction of acetone in alcohol and in the radiolysis of 2-propanol.

$$CH_3COCH_3 \xrightarrow{h\nu} (CH_3CO\ CH_3)^* \xrightarrow{CH_3CH(OH)CH_3} 2\ CH_3\dot{C}(OH)CH_3$$

$$CH_3CH(OH)CH_3 \xrightarrow{\gamma\text{-rays}} e_{solv},\ CH_3\dot{C}(OH)CH_3$$

The important role of 1-hydroxy-1-methylethyl radicals is supported by the following facts: 1) the presence of N_2O, an effective electron scavenger, has a slight effect on the radiation-induced reaction; in this case, electrons are converted into 1-hydroxy-1-methylethyl radicals and the reactive species consists mostly of 1-hydroxy-1-methylethyl radicals,

$$e_{solv} \xrightarrow{N_2O\quad (H^+)} \cdot OH \xrightarrow{CH_3CH(OH)CH_3} CH_3\dot{C}(OH)CH_3$$

2) the radical reaction initiated by benzoyl peroxide (the reflux of **1** (0.4 mmol) in 2-propanol (50 cm^3) in the presence of benzoyl peroxide (0.4 mmol)) gives **3**, although the yield is low (0.2%) probably because of the predominance of the induced decomposition of benzoyl peroxide, and 3) in the photoreaction in the presence of acetone, 2,3-dimethyl-2,3-butanediol, a coupling product from 1-hydroxy-1-methylethyl radicals, was identified.

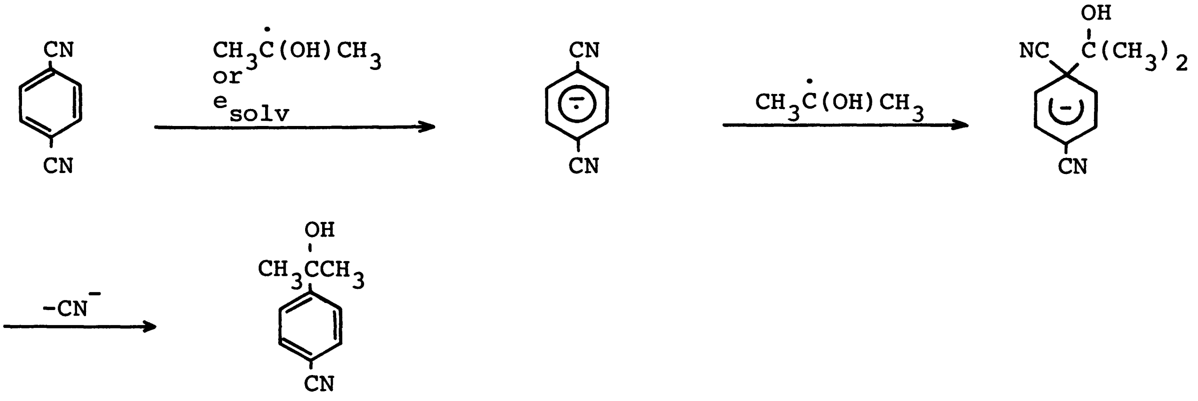
The view that a triplet state of **1** does not participate is supported by the fact that benzene does not promote the substitution.

The slight effect of N_2O on the radiation-induced reaction (Table 2) also indicates that solvated electrons are as effective as 1-hydroxy-1-methylethyl radicals for the substitution.

In the system where hydroxyalkyl radicals with higher oxidation potential are formed, the addition of N_2O lowers this type of radiation-induced reaction: for the reaction in methanol ($E_{1/2}$ vs. SCE for $\cdot CH_2OH$, -0.98 V; $E_{1/2}$ vs. SCE for

$(CH_3)_2\dot{C}OH$, -1.30 V[9]), G-values for the substitution in the absence and in the presence of N_2O are 0.16 and 0.10, respectively. This can be explained by the less efficient electron transfer from hydroxymethyl radicals than from 1-hydroxy-1-methylethyl radicals and from solvated electrons.

Considering the mechanism proposed for the photochemical substitution initiated by the elctron transfer via the excitation of CT-complexes and via exciplexes, a reaction mechanism involving the electron transfer from hydroxyalkyl radicals is plausible.



The photo-alcoholysis originates probably from a singlet excited state, because benzene and acetone do not promote (rather inhibit) the alcoholysis.

Table 1. Photochemical reactions of p-dicyanobenzene in 2-propanol
[p-Dicyanobenzene] = 0.01 mol dm^{-3}

Light source[a]	Irr. time h	Additive	[Additive] mol dm^{-3}	Conversion %	Yield of product[b] %	
					2	3
LP	5	———	———	20	35	2
LP	5	Benzene	0.22	23	7	trace
LP	3	Acetone	1.4	96	—	55
HP	3	———	———	10	—	1
HP	3	Acetone	1.4	62	—	41

a) LP, Low pressure mercury lamp; HP, High pressure mercury lamp
b) The yield is based on the consumed 1 .

Table 2. Radiation-induced reaction of p-dicyanobenzene in 2-propanol
[p-Dicyanobenzene] = 0.01 mol dm^{-3}

Additive	Dose rate rad h^{-1}	Irr. time h	G(3)[c]
———	5×10^5	20	0.60
N_2O saturated	5×10^5	20	0.63

c) G-value; Radiation chemical yield, number of molecules formed for 100 eV of radiation energy absorbed by the system

References and Notes

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6) Identification of the products was done based on the following data. Isopropyl p-cyanobenzimidate(**2**) was obtained as a mixture with isopropyl p-cyanobenzoate. Mass spectra recorded on GC-MS (Model D 300 of Nihon Denshi Co.); MS (CI method using isobutane), m/z 189 (M+1); MS (23 eV), m/z (rel intensity), 147(40), 131(7), 130(100), and 129(30). Found: m/z 129.0431. Calcd for $C_8H_5N_2$ (M - C_3H_7O): 129.0451. The IR and NMR spectra ascribed to **2** are as follows. IR (KBr disk); 3350(NH), 2210(C≡N), 1630(C=N), and 1060 cm^{-1}(C-O); NMR ($CDCl_3$) δ= 7.86 (2H, d, J = 8.2 Hz, ring H), 6.88 (2H, d, J = 8.2 Hz, ring H), 5.15 (m, J = 6.0 Hz, $(CH_3)_2C\underline{H}O$), and 1.40 (6H, d, J = 6.0 Hz, CH_3). Compound **2** is easily converted into isopropyl p-cyanobenzoate.

2-(p-Cyanophenyl)-2-propanol(**3**). Liquid; IR (direct), 3450(OH) and 2220 cm^{-1}(C≡N); NMR ($CDCl_3$) δ = 7.57 (4H, ring H), 2.70 (1H, OH), and 1.56 (6H, s, CH_3); MS (70 eV), m/z (rel intensity), 161(M^+, 5), 147(25), 146(100), 130(10), 116(9), 104(9), 102(16), 77(8), 76(11), 75(10), 59(12), 51(55), 50 (10), and 43(100). Found: m/z 146.0620. Calcd for C_9H_8N (M - CH_3) 146.0607. p-Cyanophenylmethanol was identified by the comparison of its IR and NMR spectra with those of **3** .

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