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# Successive Photosubstitution of Hexachlorobenzene with Cyanide Ion

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**Abstract:** We report a novel nucleophilic polysubstitution reaction of hexachlorobenzene (HCB) with cyanide ion in acetonitrile/water. Successive photocyanations of HCB occur with high quantum yield ($\phi_{diss} \rightarrow 0.18$) without the need for an electron acceptor, to give as products pentacyanophenol, 4-chloro-2,3,5,6-tetracyanophenol, and a dichlorotricyanophenol. The phenol functional group is introduced by competing hydrolysis of the polycyanochlorinated benzenes. Sensitization and quenching experiments indicate a triplet reactive excited state. Variation of $[CN^-]$ at constant [HCB] follows the expected relationship $\phi_{diss}{}^{-1} \propto [CN^-]^{-1}$, but variation of [HCB] at constant $[CN^-]$ shows that the reaction becomes less efficient with increasing [HCB], consistent with the formation of an unproductive excimer.

## Introduction

Photocyanation has played an important role in shaping our understanding of nucleophilic aromatic photosubstitution. As a nucleophile that is not easily oxidized, $CN^-$ encourages substitution by the $S_N2Ar^*$ mechanism,[1] whereas oxidizable nucleophiles promote a formal nucleophilic substitution by an electron-transfer mechanism.[2,3] Cyanide ion is also notable for its ability to replace hydrogen in aromatic compounds, under conditions that favor one-electron oxidation of the photoexcited aryl substrate[4,5] prior to attack by $CN^-$. Few examples have been disclosed in which cyanide replaces a halogen substituent,[6,7] and these examples are presently limited to monohalogenated aromatic compounds. In this paper we report a novel photosubstitution between hexachlorobenzene (HCB) and $CN^-$ in aqueous acetonitrile; successive photochemical replacement occurs with quantum yield > 0.1, affording highly cyanated phenolic products.

## Results and Discussion

**Product Identification.** Irradiation of HCB at 300 nm in aqueous acetonitrile in the presence of excess NaCN resulted in rapid disappearance of the title compound and the formation of a highly polar (TLC) yellow-green fluorescent product mixture. The crude product showed IR stretching bands at $\nu = 2203$ and $2176\ cm^{-1}$ ($C{\equiv}N$), but $^1H$ NMR showed no signals apart from residual solvent. The products could not be analyzed by GC or GC-MS but were successfully analyzed by negative ion electrospray MS (ES-MS). Three tentative parent ions $[M-H]^-$ were found at *m*/*z* 218 (no chlorine), 227 (one chlorine), and 236 (two chlorines). MS/MS experiments on each of the tentative parent ions showed loss of Cl for *m*/*z* 227 and consecutive loss of two chlorines for *m*/*z* 236; loss of CO $[M-H-28]^-$, characteristic for phenolic compounds,[8] was observed for all three parent ions. The possibility that one or more acetonitrile moieties might be present in the products was eliminated by showing that the product composition was unchanged when propionitrile replaced acetonitrile in the solvent. Furthermore, photolysis of HCB in the presence of $KC^{15}N$ led to the mass spectral peaks at *m*/*z* 218, 227, and 236 being displaced to *m*/*z* 223, 231, and 239, corresponding to the incorporation of 5, 4, and 3 cyano groups, respectively. The foregoing evidence suggested that the three products were pentacyanophenol (**1**, *m*/*z* 218), a tetracyanochlorophenol, and a tricyanodichlorophenol, respectively. The substance having *m*/*z* 227 was isolated and, after crystallization with much difficulty, was identified by X-ray diffraction as the sodium salt of 4-chloro-2,3,5,6-tetracyanophenol, **2** (Figure 1). Compound **3**, having *m*/*z* 236, was isolated but could not be crystallized.

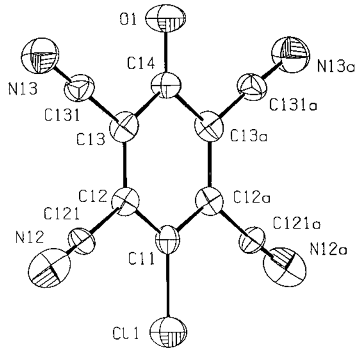

**Figure 1.** An ORTEP diagram of a phenolate ion of **2**.

A product of dechlorination (pentachlorobenzene) was detected as a very minor reaction product. Its concentration increased on adding 10% isopropyl alcohol to the reaction mixture (ratio of penta- to hexachlorobenzene in the product

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**Scheme 1.** Photochemical Cyanation of HCB

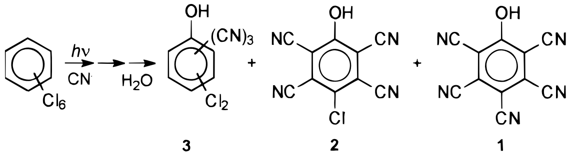


**Table 1.** Influence of Concentration of Water on Product Formation in Photolysis of HCB

| | products, %[a] | | |
|---|---|---|---|
| % water | **1** | **2** | **3** |
| 1.3 | 26 | 52 | 22 |
| 4 | 15 | 62 | 23 |
| 7 | 13 | 61 | 26 |
| 14 | 14 | 45 | 41 |

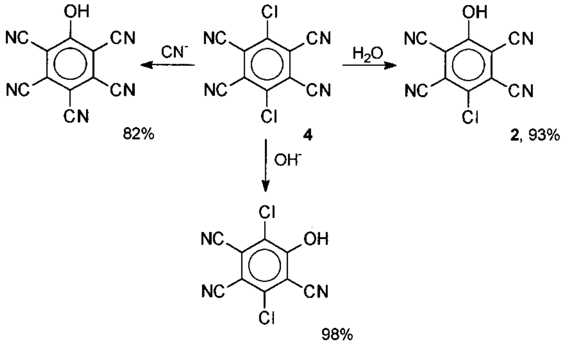
[a] Percent of phenolic products, by ES/MS.

mixture changed from 1:250 to 1:8 upon addition of isopropyl alcohol to acetonitrile/water; however, the same change (from 1:300 to 1:9) was observed in control samples without NaCN, indicating that dechlorination occurs through a minor competing pathway of C−Cl homolysis of HCB or possibly from the decomposition of an excimer of HCB).[9]

**Reaction Mechanism.** It is reasonable to assume that the products are formed by successive replacement of −Cl by −CN. We explored the possibility that the photochemical reaction is limited to formation of pentachlorobenzonitrile followed by successive thermal cyanation *o*- and *p*- to the cyano group(s). Dark controls with pentachlorobenzonitrile showed that this was not the case; the reaction involves successive photochemical steps. This observation suggests that when three or more cyano groups have been introduced into the product, hydrolysis can compete with further substitution by $CN^-$ (Scheme 1) i.e., replacement of −Cl by −OH. Alternatively, the introduction of the phenolic group may involve the replacement of −CN by −OH after at least four cyano groups are present. A precedent for the latter pathway is the slow hydrolysis of hexacyanobenzene to pentacyanophenol at elevated temperatures.[10] Either of these explanations is compatible with the observation that raising the concentration of water in the solvent system increases the concentration of **2** and **3** in the product mixture relative to **1** (Table 1); the phenolic products are resistant to further substitution of chlorine, because the phenol is immediately converted to its conjugate base. Consistent with this postulate, pentachlorophenol did not undergo any reaction even after a 24 h irradiation at 300 nm in the presence of sodium cyanide.

In an attempt to distinguish between Cl substitution and CN substitution in the formation of the phenols, we examined the hydrolysis of 1,4-dichloro-2,3,5,6-tetracyanobenzene (**4**). The reaction occurred rapidly (a few minutes) in the dark. The reaction of $OH^-$ with **4** resulted in the formation of 2,5-dichloro-3,4,6-tricyanophenol, in which −CN, but not −Cl, was substituted by hydroxide (Scheme 2). However, in acetonitrile/10% water, hydrolysis of **4** took the alternative route (replacement of Cl by water), and 93% of **2** was detected in the product mixture. When **4** was treated with $CN^-$ in acetonitrile/water mixture (9:1), pentacyanophenol (**1**) was a major product, and only 18% of **2** was detected in the product mixture. Similar trends were observed when a trichlorotricyanobenzene was reacted with water, $OH^-$ and $CN^-$ (Table 2).

**Scheme 2.** Dark Control Reactions of 1,4-Dichloro-2,3,5,6-tetracyanobenzene (**4**)



Photocyanations of aromatic hydrocarbons in acetonitrile solution are known to proceed via the singlet excited state in the presence of electron acceptors but via triplet excited-state excimers in the absence of electron acceptors.[11] The reported quantum yield of intersystem crossing for HCB is 0.5,[12] consistent with either singlet or triplet state reactivity. The following observations indicate a triplet state reaction. The rate of photocyanation was 2-fold faster in degassed than in aerated solution, and sensitization of the HCB/$CN^-$ reaction ($E_T$ of HCB is 307 kJ/mol)[12] could be achieved by acetone ($E_T = 332$ kJ/mol)[12] or acetophenone ($E_T = 311$ kJ/mol).[12] A triplet was shown to be the only reactive excited state in the process of interest, since a Stern−Volmer plot of the quenching of HCB by ferrocene ($E_T = 159$ kJ/mol)[12] was linear: $\phi_o/\phi_q = 1.27 + 879[\text{Ferrocene}]$, $r^2 = 0.968$.

**Reaction Kinetics.** The overall disappearance of HCB follows pseudo-first-order kinetics ($\ln\{[\text{HCB}]_o/[\text{HCB}]_t\} \propto t$) with apparent rate constants ranging from $1.1 \times 10^{-3}$ to $6.7 \times 10^{-5}$ $s^{-1}$ depending on the concentrations of water and sodium cyanide. The absolute quantum yield for the disappearance of HCB ($\phi_{diss}$) was difficult to determine because the products are much more strongly absorbing than the starting material;[13] in addition, sodium chloride, a reaction byproduct, forms a mist which causes substantial light scattering. Extrapolation of the apparent $\phi_{diss}$ to zero time at $[\text{NaCN}] = 0.324$ mol $L^{-1}$ and $[\text{HCB}] = 3.88 \times 10^{-4}$ mol $L^{-1}$ in 95:5 acetonitrile:water mixture gave a limiting quantum yield of 0.14 at 313 nm (Figure 2). A notable feature of the reaction is that the subsequent photocyanation steps must each proceed with $\phi_{diss} > 0.14$, because no intermediate products such as pentachlorobenzonitrile or tetrachlorodicyanobenzene are detected in the product mixture. Therefore the total photon efficiency must be very high, although we cannot quantify it.

Photocyanations in the absence of added electron acceptors can take place through the intermediacy of an excimer,[6,14] such that attack on the excimer by nucleophile permits charge to be removed from the excimer in the form of the anion radical. To investigate whether an HCB excimer was involved in product formation, we measured $\phi_{diss}$ as a function of HCB concentration. The plot of $\phi_{diss}^{-1}$ vs (initial $[\text{HCB}])^{-1}$ (Figure 3) had a negative slope ($-4.15 \pm 0.34 \times 10^{-5}$ mol $L^{-1}$), indicating that although an excimer of HCB is indeed formed upon irradiation, it is unreactive. A precedent for an unreactive excimer exists

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**Table 2.** Product Formation in Ground State Reactions of Chlorinated Polycyanobenzenes

| products (%): | reagent | | | | | |
|---|---|---|---|---|---|---|
| | water | | NaOH | | NaCN | |
| | $C_9Cl_3N_3$[b] | $C_{10}Cl_2N_4$[b] | $C_9Cl_3N_3$[b] | $C_{10}Cl_2N_4$[b] | $C_9Cl_3N_3$[b] | $C_{10}Cl_2N_4$[b] |
| **1** | | | | | | 82 |
| **2** | 10 | 93 | 5 | 2 | 15 | 18 |
| $C_9Cl_2N_3OH$[a] | 74 | 7 | 63 | 98 | 10 | |
| *m/z* 245 | 16 | | 32 | | | |

[a] This compound cannot be identified as **3**. [b] Reagent.

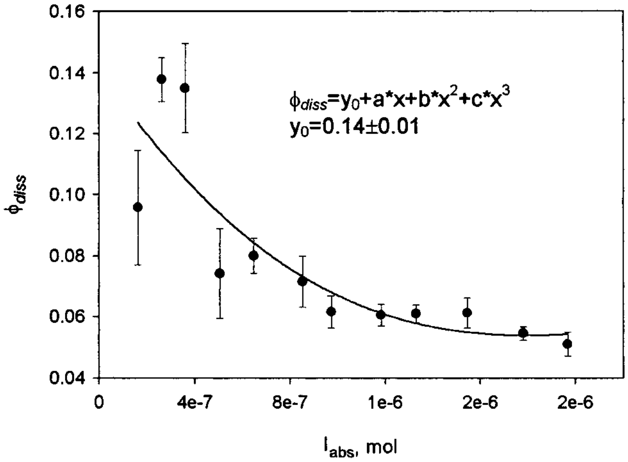

**Figure 2.** Estimation of a quantum yield for disappearance of HCB.

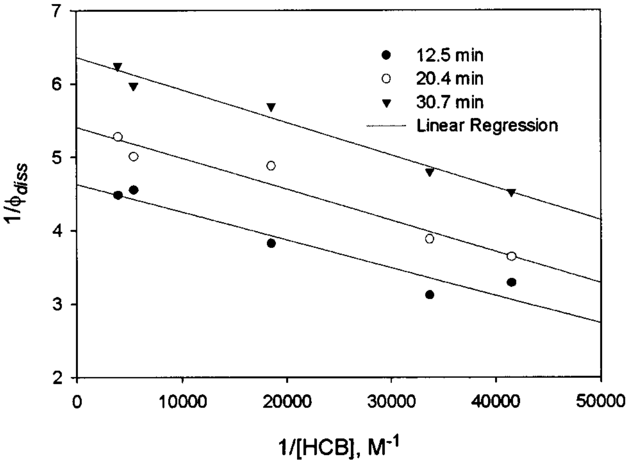

**Figure 3.** Double reciprocal plot of $\phi_{diss}$ versus [HCB]. The three sets of lines represent data points taken at different stages of the reaction; the apparent $\phi_{diss}$ changes with percent conversion as shown in Figure 2.

**Table 3.** Influence of Concentration of Water on Percent Conversion of HCB at Equal Irradiation Times

| % water | % convn of HCB[a] | $\phi_{diss}$[b] |
|---|---|---|
| 1.3 | 70 | 0.18 |
| 4.6 | 55 | 0.14 |
| 7.97 | 41 | 0.11 |
| 14.6 | 24 | 0.06 |

[a] Initial concentration of HCB was $1.67 \times 10^{-4}$ M, with [NaCN] = 0.131 M. [b] Apparent $\phi_{diss}$, not extrapolated to zero conversion.

in the homolysis of chlorobenzene, the quantum yield of which decreases with increasing [PhCl].[15]

The reaction between photoexcited HCB and $CN^-$ was, as expected, first order in each reactant, as shown by linear plots of apparent $\phi_{diss}^{-1}$ vs $[NaCN]^{-1}$ ($\phi_{diss}^{-1} = 3.4 + 0.74\,[NaCN]^{-1}$, $r^2 = 0.986$) when [HCB] = $3.74 \times 10^{-4}$ mol $L^{-1}$. Increasing the water content of the aqueous acetonitrile at constant $[CN^-]$ significantly reduced $\phi_{diss}$, on account of the decrease in the ratio $CN^-$:$OH^-$ (Table 3).

The foregoing experiments led us to write Scheme 3 as the tentative mechanism for photocyanation of HCB. The products are proposed to form from the triplet excited state of HCB, most likely via the $S_N2(Ar^*)$ mechanism, with excimer formation acting as an unproductive side reaction. The minor amount of homolysis has not been included in Scheme 3.

## Scheme 3

$$\begin{array}{rl}
\mathrm{ArCl} \rightarrow {}^1\mathrm{ArCl}^* & I_{abs} \\
{}^1\mathrm{ArCl}^* \rightarrow \mathrm{ArCl} & k_1 \\
{}^1\mathrm{ArCl}^* \rightarrow {}^3\mathrm{ArCl}^* & k_2 \\
{}^3\mathrm{ArCl}^* \rightarrow \mathrm{ArCl} & k_3 \\
{}^3\mathrm{ArCl}^* + \mathrm{CN}^- \rightarrow \text{products} & k_4 \\
{}^3\mathrm{ArCl}^* + \mathrm{ArCl} \rightarrow \text{excimer} & k_5 \\
\text{excimer} \rightarrow 2\ \mathrm{ArCl} &
\end{array}$$

Equation 1 gives the rate of disappearance of HCB, and eq 2 is the relationship between $\phi_{diss}^{-1}$ and $[NaCN]^{-1}$. Equation 1 takes into account the conditions under which these experiments were carried out, namely low light absorption by HCB. Consequently, the rate of product formation increases with [HCB], even though the excimer is not reactive, simply because more light is absorbed. It was therefore necessary to make a careful determination of light absorbed at each concentration of HCB before computing $\phi_{diss}$.

$$\text{rate} = \frac{2.303 I_0 \epsilon_{HCB} l k_2 k_4 [HCB][CN^-]}{(k_1 + k_2)(k_2 + k_4[CN^-] + k_3[HCB])} \qquad (1)$$

$$\frac{1}{\phi_{diss}} = \left(1 + \frac{k_1}{k_2}\right)\left(1 + \frac{k_3 + k_5[HCB]}{k_4[CN^-]}\right) \qquad (2)$$

Note that a reaction scheme in which the excimer lies on the route to product gives the relationship $\phi_{diss}^{-1} \propto [HCB]^{-1}$, with the slope being positive (cf. Figure 3).

The parameter intercept/slope from eq 2 had the value 4.72; this parameter is $k_4/(k_3 + k_5[HCB])$, from which the ratio of $^3$HCB molecules that are trapped by $CN^-$ can be calculated for any concentration of $CN^-$ and HCB. At $[CN^-]$ = 0.324 mol $L^{-1}$ and [HCB] = $2.56 \times 10^{-4}$ mol $L^{-1}$, this ratio is 0.6.

## Conclusions

Several mechanisms for nucleophilic substitution of aryl halides have been proposed, namely $S_N2(Ar^*)$, $S_{R+N}1(Ar^*)$, and electron transfer.[6] The results of our study are most readily accommodated by the $S_N2(Ar^*)$ reaction, in which a Meisenheimer complex is formed between the excited substrate and nucleophile, followed by departure of the substituent from the complex. The $S_{R+N}1(Ar^*)$ mechanism, with ionization of the excited aromatic to a radical cation, is followed mainly for the molecules activated by electron-donating groups. Examples include photosubstitution of chlorobenzene[14] and photocyanation of chloro- and fluoroanisoles.[6] In the electron transfer reaction, which is promoted particularly in polar solvents, the formation of radical cations proceeds via an electron transfer from the excited aromatic to a ground state electron acceptor. It seems unlikely that an electron-deficient compound such as HCB would form a radical cation, and no obvious electron donors are present to produce a radical anion.

The novel aspects of this research are the discovery of the nonexcimer mediated photocyanation of a polychlorinated aromatic without the assistance of an added electron acceptor and the observation of multiple photosubstitution steps, each proceeding with high efficiency. The reaction reported here is not unique to HCB but seems to be common to a wide variety of polyhaloaromatic compounds. We are currently extending this work to the study of successive photochemical cyanations on lower chlorinated benzenes, highly chlorinated polycyclic aromatics, such as biphenyls, naphthalenes, and dioxins, and polyfluorinated aromatic compounds.

## Experimental Section

**General Methods.** HPLC grade acetonitrile, methanol, and ethyl acetate were obtained from Fisher. All solvents were used as received. Potassium cyanide $^{15}N$ (99%+ isotopic purity) was purchased from Isotech Inc. Hexachlorobenzene (Aldrich) was twice recrystallized from chloroform/methanol before use.

**Irradiations.** Solutions of HCB and NaCN were photolyzed in 8 mm o.d. Pyrex test tubes in a Rayonet RPR photochemical reactor equipped with 16 RPR-3000 low-pressure mercury lamps which emit a band at 300 nm with a bandwidth of 25 nm at a half-intensity. When necessary, samples were degassed and sealed on a vacuum manifold using four freeze−pump−thaw cycles (last two cycles using an oil-diffusion pump, $P < 0.01$ Torr).

**Measurement of Quantum Yield of Disappearance of HCB.** Quantum yields of substrate disappearance were determined by potassium ferrioxalate actinometry[16] using solutions of potassium chromate and nickel sulfate[17] as a filter. The actinometer in water and the test solution in acetonitrile, containing 5% water, were placed in 8 mm o.d. Pyrex test tubes which were positioned coaxially in 25 mm o.d. Pyrex test tubes filled with optical filter. The filter transmitted in the 285−335 nm region, with maximum transmittance of approximately 20% at 313 nm. The actinometer and test solutions were irradiated simultaneously in the photoreactor using a merry-go-round to ensure equal light intensity incident on all solutions. All the light was absorbed by the actinometer, and the photon intensity absorbed by the actinometer ($I_o = 7.09 \times 10^{-7} \pm 7.55 \times 10^{-8}$ mol min$^{-1}$) was calculated based on $\phi_{313} = 1.24$ for potassium ferrioxalate.[12]

The intensity absorbed by the test solution was determined in a separate experiment. Solutions of HCB ($3.88 \times 10^{-4}$ mol L$^{-1}$, $A_{313} = 0.01$) acetonitrile/water (5% $H_2O$) were degassed, sealed under vacuum, and irradiated for various time intervals, ranging from 10 min to 2 h. After irradiation, the ampules were opened, and disappearance of HCB was determined by HPLC analysis. The apparent quantum yields were calculated and plotted against $I_{abs}$.

**Sensitization of HCB Photocyanation by Acetone, Acetophenone, and Oxygen Removal.** Concentrations of acetone and acetophenone were chosen such that most of the incident light was absorbed by the sensitizers. Eight solutions of HCB ($2.73 \times 10^{-4}$ M) in acetonitrile/water (5% $H_2O$), containing NaCN ($8.06 \times 10^{-2}$ M) were prepared, with two having acetone (0.125 M, $A_{300} = 0.78$) and the other two having acetophenone ($1.12 \times 10^{-2}$ M, $A_{300} = 0.57$) added. Six samples and two more without sensitizers were degassed and sealed under vacuum. The duplicate samples were irradiated at 300 nm for 7 min and analyzed by HPLC (Table 4).

**Table 4.** Sensitization of HCB Photocyanation by Acetone, Acetophenone, and Oxygen Removal

| sample | $C_{reacted}$, M | ratio $C_i/C_{aerated}$ | % convn |
|---|---|---|---|
| aerated | $6.47 \times 10^{-5} \pm 5.6 \times 10^{-6}$ | 1 | 25 |
| degassed | $1.52 \times 10^{-4} \pm 5.6 \times 10^{-6}$ | 2.35 | 54 |
| acetone | $2.42 \times 10^{-4} \pm 3.6 \times 10^{-6}$ | 3.74 | 87 |
| acetophenone | $2.67 \times 10^{-4} \pm 6.63 \times 10^{-6}$ | 4.13 | 99 |

**Quenching of HCB Photocyanation by Ferrocene.** Photolyses were done in acetonitrile, containing 5% water, with the initial concentrations of HCB and sodium cyanide equal to $1.67 \times 10^{-4}$ and 0.131 M, respectively. Degassed samples were irradiated for 20 min and analyzed by HPLC. The Stern−Volmer plot was obtained by plotting the ratio of quantum yields of reaction in the absence of the quencher to that in the presence of the quencher ($\phi_o/\phi_q$) versus the concentration of quencher.

**Photolysis of HCB at Various Concentrations of Sodium Cyanide.** Nondegassed solutions of HCB ($2.56 \times 10^{-4}$ M) in acetonitrile/water (5%), having various concentrations of sodium cyanide, were irradiated for 30, 50, and 80 min at 300 nm. Values for $\phi_{diss}$ were calculated for each run and averaged.

**Synthesis and Ground-State Reactions of 1,4-Dichloro-2,3,5,6-tetracyanobenzene and a Trichlorotricyanobenzene.** To the mixture of dichlorotricyanophenol **3** (3.1 mg) and phosphorus oxychloride (0.1 mL) at room temperature was added 14 $\mu$L of freshly distilled pyridine. The reaction mixture was heated at 80 °C for 7 min, cooled to 25 °C, and poured onto ice/water mixture (2.0 mL). Upon standing (45 min) a precipitate was formed, filtered under vacuum, washed with a small amount of cold water, and dried. The product was identified as a trichlorotricyanobenzene by GC-MS: yield 1.8 mg. Chlorination of 1.8 mg of **2** by the same procedure yielded ca. 0.8 mg of 1,4-dichloro-2,3,5,6-tetracyanobenzene **4**.

The chlorination products were dissolved in acetonitrile (10.0 mL) and 1.0 mL aliquots were mixed with 1.0 mL solutions of NaCN in acetonitrile/water (0.262 M, 10% $H_2O$), NaOH in water (2.5%), and deionized water, respectively, at room temperature. The progress of reactions was monitored by HPLC, and the mixtures were subjected to ES-MS analysis after 1 h.

**Large-Scale Photolysis of HCB.** In a typical experiment 100 mg (0.35 mmol) of HCB and 450 mg (9.2 mmol) of NaCN were dissolved in 250 mL of acetonitrile, containing 5% water using a model FS-3 sonicator (Fisher). The solution was placed into four 25 mm o.d. Pyrex test tubes and irradiated for 8 h at 300 nm in a merry-go-round. The combined solutions were extracted with hexane (3 × 70 mL) and stirred in a well ventilated fume cabinet at room temperature in the presence of 5.6 g of Dowex 50W (50X4−100, Sigma). The solution was stirred for additional 30 min at 50 °C to remove dissolved hydrogen cyanide. Upon cooling to room temperature, the resin was removed by a vacuum filtration. The solution was dried overnight over activated 4 Å molecular sieves. After drying and filtering, acetonitrile was removed on a rotary evaporator; the residue was taken up on 5 g of silica gel (60−200 mesh), which was then placed onto a bed of preequilibrated silica gel and eluted with ethyl acetate−acetonitrile mixture (4:1). Collected fractions (typically 15 fractions of 10−12 mL) were subjected to analysis by TLC and combined, if similar. The purity of isolated products was checked by ES-MS. The hexane extracts were shown to contain only unreacted HCB with a typical recovery of ca. 40 mg of the starting material. The products **2** and **3** were isolated with 60% raw yield based on reacted HCB.

**2,3,4,5,6-Pentacyanophenol (not isolated).** Mass spectrum, *m/z* (%) 218 (M−H) (100), 219 (13.9), 220 (1.9); MS/MS, Daughters of *m/z* 218: *m/z* (%) 190 (46), 164 (5.1), 138 (2.6), 114 (46.2).

**4-Chloro-2,3,5,6-tetracyanophenol (2) (sodium salt).** Approximately 20 mg (38% yield, based on reacted HCB) was obtained with

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93% purity (ES-MS) as a yellow solid turning fluorescent-green in solution, mp 381−384 °C (decomp.), $^{13}$C NMR ($CD_3CN$): $\delta$ 113.25, 114.08, 114.66*, 115.50*, 115.83, 116.12*, 117.85, 122.19*, 122.48, 171.46 (* - impurity from **3**); Mass spectrum, $m/z$ (%) 227 (M−H) (100), 228 (12), 229 (34.1), 230 (4.2); MS/MS, Daughters of $m/z$ 227 (M−H): $m/z$ (%) 199 (16.7), 192 (15.2), 164 (49.9), 151 (1.9), 138 (9.6), 123 (6.6).

**A Dichlorotricyanophenol (3) (sodium salt).** Approximately 15 mg (25% yield) was obtained with 90% purity (ES-MS). A yellow solid, stays yellow in solution, mp 192−194 °C (decomp.), $^{13}$C NMR ($CD_3CN$): $\delta$ 107.69, 114.10 (impurity from **2**), 114.60, 115.78, 116.13, 119.29, 122.19, 131.81, 141.50, 171.02; Mass spectrum, $m/z$ (%) 236 (M−H) (100), 237 (12.4), 238 (63.5), 239 (7.7), 240 (11.1); MS/MS, Daughters of $m/z$ 236 (M−H): $m/z$ (%) 208 (6.5), 201 (6.2), 173 (16.5), 166 (16.1), 138 (54.7).

**Acknowledgment.** We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

**Supporting Information Available:** Details of the HPLC, ES-MS, NMR, GC-MS, and X-ray crystallographic methods, an ORTEP diagram of the asymmetric unit of **2**, and an X-ray crystallographic file for **2**, in CIF format (20 pages, PDF/print). See any current masthead page for ordering information and Web access instructions.

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