

and to Professor James Trotter for the use of the diffractometer and structure-solving programs.

**Supplementary Material Available:** Experimental details for the preparation of  $\text{Ir}(\text{CH}_2)[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]$ ,  $^1\text{H}$  NMR and microanalytic data for all new compounds, tables of final positional and isotropic thermal parameters, calculated hydrogen coordinates, final anisotropic thermal parameters, bond lengths, bond angles, intraannular torsion angles, torsion angles, and structure factor amplitudes (observed and calculated) (47 pages). Ordering information is given on any current masthead page.

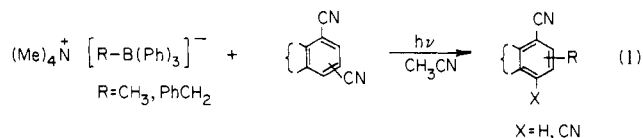
## Photoalkylation of Dicyanoarenes with Alkyltriphenylborate Salts

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Received June 17, 1985

The promising synthetic utility of light-induced single-electron-transfer (SET) reactions has been partly realized in the generation of stabilized radicals by oxidation of olefins,<sup>1</sup> amines,<sup>2</sup> silanes,<sup>3</sup> or stannanes<sup>4</sup> with following loss of an electrophilic group. Herein we introduce a new class of photooxidizable reagents, alkyltriphenylborates, that enable the facile transfer of an alkyl group to an electron acceptor. Irradiation of acetonitrile solutions of dicyanoarenes and either methyl- or benzyltriphenylborate gives good yields of alkylcyanoarenes, eq 1.



The preparation of methyl- (**1**) or benzyltriphenylborate (**2**) proceeds smoothly from the alkylolithium and triphenylboron.<sup>5</sup> The borates are easily isolated as their crystalline tetramethylammonium salts.<sup>6</sup> These salts are stable in air and protic solvents and are soluble in acetonitrile.

The electrochemical oxidation of tetra-*n*-butylborate is reported to generate the butyl radical.<sup>7</sup> The cyclic voltammograms of borates **1** and **2** exhibit irreversible one-electron oxidation waves at ca. 1.11 and 0.85 V vs. SCE, respectively. We suspect that cleavage of the alkyl carbon-boron bond<sup>8</sup> follows oxidation of **1** or **2**.

The fluorescence of 1,4-dicyanonaphthalene (DCN) is quenched by borate **2** with a bimolecular rate constant at the diffusion limit ( $1.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  in  $\text{CH}_3\text{CN}$ ). This finding is not unexpected since the free energy of electron transfer from **2** to  $\text{DCN}^{\bullet-}$  is exothermic by more than 30 kcal/mol.<sup>9</sup> The generation of  $\text{DCN}^{\bullet-}$  in this reaction is confirmed by measurement of its characteristic absorption spectrum using laser flash photolysis techniques.<sup>10</sup>

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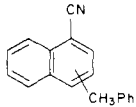
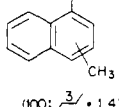
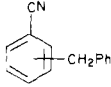
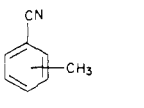
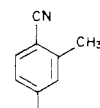
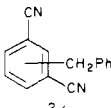
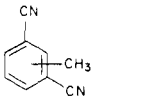
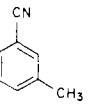
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Table I. Product Distribution of Photoreaction between Borate (**1** or **2**) and Dicyanoarene (DCN, *p*-DCB, or *m*-DCB)

[R-BPh <sub>3</sub> ] <sup>-</sup> [N(CH <sub>3</sub> ) <sub>4</sub> ] <sup>+</sup>	Ar(CN) <sub>2</sub>	conv, % <sup>a</sup>	product, % <sup>b,c</sup>
R = PhCH <sub>2</sub>	DCN	78	 (95: 3/4 - 0.6)
R = CH <sub>3</sub>	DCN	65	 (100: 3/4 - 1.4)
R = PhCH <sub>2</sub>	<i>p</i> -DCB	38	 (79: ortho/para=0.1)
R = CH <sub>3</sub>	<i>p</i> -DCB	21	 (69: ortho/para=0.4)  (27)
R = PhCH <sub>2</sub>	<i>m</i> -DCB	59	 (85: 2/4 - 0.1)
R = CH <sub>3</sub>	<i>m</i> -DCB	71	 (95: 2/4 - 0.12)  (5)

<sup>a</sup> Conversions are based on loss of borates for DCN and on loss of dicyanoarenes for *p*-DCB and *m*-DCB. <sup>b</sup> The yields are determined by gas chromatography except for **2** and *p*-DCB where the products were isolated. <sup>c</sup> A low yield of toluene is obtained from all reactions of **2**.

Irradiation (350 nm) of DCN (11.2 mM) in deoxygenated acetonitrile containing methylborate **1** (8.3 mM) gives two methylated cyanonaphthalenes in essentially quantitative yield, Table I. The methylcyanonaphthalenes were isolated by chromatography and identified as 3- and 4-methyl-1-cyanonaphthalene in a ratio of 7:5 by comparison with authentic material independently prepared.<sup>11</sup> Similarly, photolysis of DCN in acetonitrile solution containing benzylborate **2** gives a 95% yield of 3- and 4-benzyl-1-cyanonaphthalene<sup>13</sup> in this case, however, the former isomer is the minor product. A low yield of toluene is also observed in this reaction.

The issue is slightly more complex when *m*- or *p*-dicyanobenzene (*m*-DCB, *p*-DCB) is photolyzed in place of DCN. Irradiation (Hg arc, Pyrex) of *p*-DCB in the presence of methylborate **1** gives

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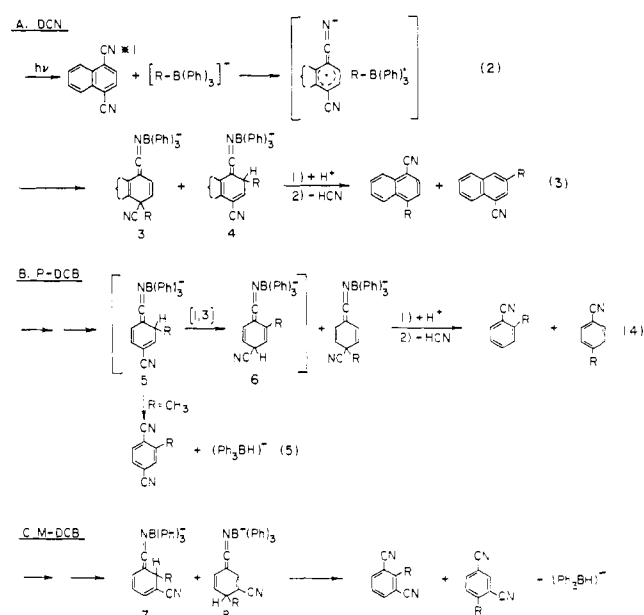
(11) The preparation of 4-methyl-1-cyanonaphthalene<sup>12</sup> proceeds from 1-methyl-4-bromonaphthalene and CuCN:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.74 (3 H, s), 7.2-8.3 (6 H, m); mp 53-54 °C. The 3-methyl-1-cyanonaphthalene<sup>12</sup> was prepared by the Pd-catalyzed coupling of 2-bromophenylacetonitrile and methyl alcohol with following dehydration and oxidative aromatization: NMR ( $\text{CDCl}_3$ )  $\delta$  2.54 (3 H, s), 7.5-8.3 (6 H, m).

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(13) The benzylcyanonaphthalenes were identified from spectral data. 4-Benzyl-1-cyanonaphthalene:<sup>14</sup> mass spectrum EI (70 eV), *m/e* 243, 228, 91; exact mass calcd for  $\text{C}_{18}\text{H}_{13}\text{N}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  4.43 (2 H, s), 7.0-8.4 (11 H, m). 3-Benzyl-1-cyanonaphthalene: mass Spectrum EI (70 eV), *m/e* 243, 228, 91; exact mass calcd for  $\text{C}_{18}\text{H}_{13}\text{N}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  4.09 (2 H, s), 7.0-8.4 (11 H, m).

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Scheme I



*o*- and *p*-toluonitrile and 2-methyl-1,4-dicyanobenzene (Table I). In this case, the transferred methyl group has been substituted for either a cyano group or a hydrogen on the original dicyanoarene. The same phenomenon is observed for *m*-DCB, but in this instance formation of alkylidicyanobenzenes accounts by far for the chief products. Similar results are obtained when benzylborate **2** is used.

It is possible from the results described above to formulate a tentative mechanistic rationale. This proposal is outlined in Scheme I. The first steps in the mechanism are common to all of the dicyanoarenes we examined and are illustrated for DCN. Irradiation creates the excited singlet of the arene which is quenched by electron transfer to generate the dicyanoarene radical anion<sup>15</sup> and an alkyltriphenylboron radical. Eventual cleavage<sup>7,8</sup> of the oxidized borate at the bond between the alkyl carbon and boron releases the alkyl group and triphenylboron. We suggest these components combine with DCN<sup>-</sup> to form the isomeric ketiminoborates **3** and **4** (eq 3). Protonation and dehydrocyanation complete the reaction sequence and generate the observed products.

The ketiminoborates formed from *p*- and *m*-DCB apparently have alternative reaction paths available. For the former, intermediate **5** may tautomerize to **6** before protonation and dehydrocyanation releases the *o*-alkylbenzonitrile. The ketiminoborates **7** and **8** (in part **5**) must undergo an elimination of perhaps triphenylborohydride or its equivalent to form the isolated alkylated dicyanobenzene products.

The mechanism outlined in Scheme I is but one of several that can account for the observations. Additional experiments are required to define the process more clearly. Nevertheless, the potential utility of the photooxidation of alkyltriphenylborates is clear from our findings. These reagents mediate the efficient transfer of alkyl groups to excited electron acceptors. There is no reason to expect that the acceptors must be restricted to dicyanoarenes. Work is under way to define the scope of this process.

**Acknowledgment.** We thank Professor Larry Faulkner of this department for the use of cyclic voltammetric equipment and Professor J. C. Martin for a sample of 2,6-dicyanotoluene. We specially thank Professor Scott Denmark for suggesting the synthesis of 3-methyl-1-cyanonaphthalene. This work was supported by a grant from the Mead Corporation and in part by the National Science Foundation.

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**Registry No.** (Me)<sub>4</sub>N<sup>+</sup>[MeB(Ph)<sub>3</sub>]<sup>-</sup>, 98689-31-7; (Me)<sub>4</sub>N<sup>+</sup>[PhCH<sub>2</sub>B(Ph)<sub>3</sub>]<sup>-</sup>, 98689-33-9; 1,3-NCC<sub>6</sub>H<sub>4</sub>CN, 626-17-5; 1,4-NCC<sub>6</sub>H<sub>4</sub>CN, 623-26-7; 2-NCC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, 529-19-1; 4-NCC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, 104-85-8; 2-NCC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Ph, 56153-61-8; 4-NCC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>Ph, 23450-31-9; 3-NCC<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>, 620-22-4; 1,4-dicyanonaphthalene, 3029-30-9; 3-methyl-1-cyanonaphthalene, 71235-72-8; 4-methyl-1-cyanonaphthalene, 36062-93-8; 3-benzyl-1-cyanonaphthalene, 98689-34-0; 4-benzyl-1-cyanonaphthalene, 78075-59-9; 2-methyl-1,4-dicyanobenzene, 55984-93-5; 2-benzyl-1,3-dicyanobenzene, 98689-35-1; 4-benzyl-1,3-dicyanobenzene, 98689-36-2; 2-methyl-1,3-dicyanobenzene, 2317-22-8; 4-methyl-1,3-dicyanobenzene, 1943-88-0; 4-bromo-1-methylnaphthalene, 6627-78-7.

## Adsorption and Reactivity of Acetylene on a Cu(110) Surface

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Received July 1, 1985

Outka et al.<sup>1</sup> recently reported that acetylene on a Cu(110) surface is largely nondissociatively adsorbed and desorbs reversibly in a broad temperature region with peaks at 280, 340, and 375 K. Additionally, it was reported that ~340 K some disproportionation occurred to ethylene, which desorbed molecularly, and an irreversibly adsorbed carbonaceous residue which accounted for 11% of the initially adsorbed acetylene. This disproportionation to release ethylene was cited as the first reported reaction of this kind under ultrahigh vacuum conditions.

In this paper I report relevant aspects of a more extensive high-resolution electron energy loss (EEL) and thermal desorption (TD) spectroscopic study of the adsorption and reactivity of acetylene on (110) and (100) copper surfaces. In particular, this work shows that Outka et al. failed to detect the major desorption product, benzene, and appear to have erroneously attributed mass spectrometric fragments of benzene to ethylene.

Multiplexed TD spectra (2, 26, 27, 78) from a saturated surface indicated that hydrogen (2), acetylene (26), and benzene (78) were desorbed (solid lines, Figure 1). Although a small pulse of *m/e* 27 was seen, this must be attributed to mass spectrometric fragmentation of benzene and not ethylene. The contribution to the *m/e* 27 (and 26) spectra (5.5% of parent 78) from this source are shown by the dashed lines. Reaction-limited hydrogen desorption<sup>2</sup> (not shown in Figure 1) was seen in a broad region between 600 and 900 K with two poorly defined maxima near 650 and 800 K.

It is apparent from these observations that trimerization to benzene is the main surface process. Trimerization to benzene is a well-known homogeneously catalyzed reaction but only recently has been reported on low-index single-crystal surfaces of palladium<sup>3-5</sup> under ultrahigh vacuum conditions comparable to that used in the present study.

Figure 2 shows EEL spectra recorded after heating saturated monolayers of (a) C<sub>2</sub>H<sub>2</sub> and (b) C<sub>2</sub>D<sub>2</sub> to ~280 K. Prominent bands are listed and assigned in Table I. The band at 690 cm<sup>-1</sup> in the C<sub>2</sub>H<sub>2</sub> spectrum is assigned to the γ(CH) mode of coadsorbed benzene from the trimerization reaction. This assignment is in accordance with other work in this laboratory with benzene alone on Cu(110) which showed a similar dominant band near 700 cm<sup>-1</sup> and reversible desorption in a broad structureless region between 200 and 310 K. The remaining bands are assigned to nondissociatively adsorbed acetylene. These assignments follow those proposed by Bandy et al.<sup>6</sup> for C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>D<sub>2</sub> on Cu(111), the

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