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FREE RADICAL FORMATION IN THE PHOTOOXIDATIVE ALKYLATIONS OF DICYANONAPHTHALENE WITH ALKYLTRIPHENYLBORATE SALTS

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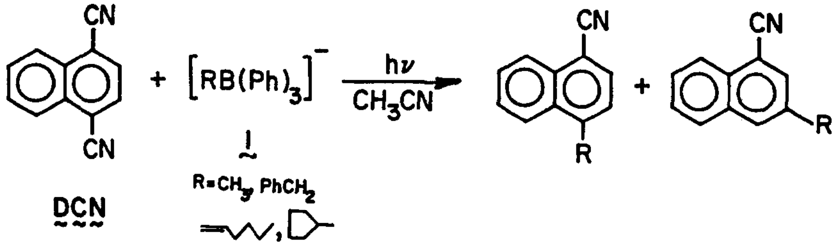
Summary: One electron oxidation of alkyltriphenylborate salts leads to carbon-boron bond cleavage and the formation of free alkyl radicals.

Photolysis of an Argon saturated acetonitrile solution of 1,4-dicyanonaphthalene (DCN) containing an alkyltriphenylborate as its tetramethylammonium salt (1) cleanly gives two isomeric alkylated 1-cyanonaphthalenes in excellent overall yield,[1] Eq. 1. Analysis of this reaction by laser spectroscopy confirmed the operation of an electron transfer mechanism generating, at least initially, $DCN^{\cdot-}$ and, presumably, the alkyltriphenyl boranyl radical (2), Eq. 2. Herein we report experiments which indicate that homolytic carbon-boron bond cleavage to generate free alkyl radicals precedes final product formation in this reaction.



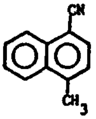
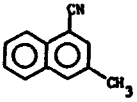
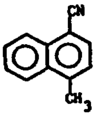
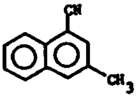
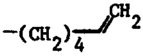
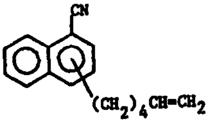
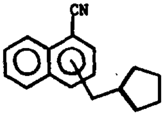
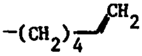
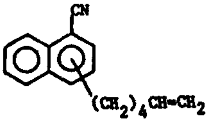
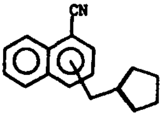
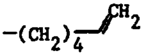
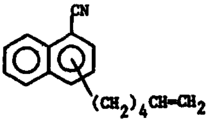
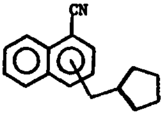
(1)

$$\mathrm{DCN}^{*} + [\mathrm{R{-}B(Ph)_3}]^{-} \xrightarrow{\mathrm{SET}} \mathrm{DCN}^{\cdot -} + \underset{2}{[\mathrm{R{-}B(Ph)_3}]^{\cdot}} \qquad (2)$$

Electron transfer between singlet excited DCN and borate 1 occurs when these reagents become neighbors in a solvent cage. Thus it is possible that the entire sequence of reactions leading to the alkylated naphthalenes is completed within this initial cage and that truly free radicals or radical ions are not involved. The operation of a totally in-cage process is attractive because it neatly accomodates the observed high product yields. Reactions of this sort that do involve freely solvated intermediates can be identified with a tandem electron transfer sequence.

The fluorescence of DCN is quenched by naphthalene at a diffusion limited rate.[2] This reaction generates $DCN^{\cdot-}$ and naphthalene radical cation, both of which can be detected spectroscopically. When a solution of DCN in acetonitrile containing borate 1 (R=Me, 9×10^{-3} $\underline{M}$) and 25-fold excess of naphthalene (0.22 $\underline{M}$) is irradiated at 350 nm (only the DCN, 0.013 $\underline{M}$, absorbs light) the 3- and 4-methyl-1-cyanonaphthalenes are formed with approximately the same yield and in the same ratio as in the absence of the naphthalene (Table 1).

Table 1. Products of Alkyl Transfer to DCN[a]

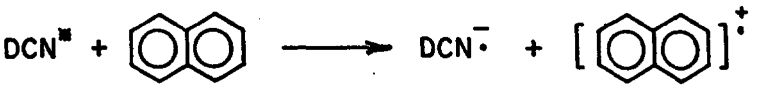
Borate $[R\text{-}B(Ph)_3]^-$	Additive -or- Light Source	Products		Ratio (yield)
$-CH_3$	None			1.25 (100%)
$-CH_3$	Naphthalene (0.22 M)			1.23 (81%)
 b	None Rayonet			1.5±0.2 (92%)
	None Laser			8±1
	Air Rayonet			4± 2

a) Typical conditions: borate (8.6 mM), DCN (11.2 mM) in CH_3CN (2 mL) irradiated in Rayonet for 30-50 min.

b) The ratio of the 3-:4- isomers of the 5-hexenyl- and cyclopentylmethyl-1-cyanonapthalenes is 1:2 throughout.

Since both naphthalene and the borate quench DCN^{*1} with the same rate constant, reaction in the presence of excess naphthalene must first form the naphthalene radical cation, Eq. 3. The oxidation potential of borate 1 is lower than that of naphthalene,[1,3] so every time a naphthalene radical cation encounters 1 it converts it to radical 2, Eq. 4. The net result is to generate $DCN^{\cdot-}$ and 2 in different solvent cages. Since the efficiency of reaction and the products of the tandem electron transfer are approximately the same as those from the direct irradiation, we can conclude with some confidence that the reaction shown in Eq. 1 need not occur entirely in the initial solvent cage.

Formation of the alkylated cyanonaphthalenes could proceed by a direct displacement of $(Ph)_3B$ from 2 by $DCN^{\cdot-}$ (S_n2-like), Eq. 5, or by initial homolytic cleavage of the



(3)

(4)

alkyl-carbon-boron bond of 2 generating a free alkyl radical (R•) followed by its combination with $DCN^{\overline{\cdot}}$ (S_n1-like), Eq. 6. These two possibilities can be distinguished by employing the cyclization of the hexenyl radical as an indicator.[4]

5-Hexenyltriphenylborate is easily prepared from the alkenyllithium and triphenylboron.[5] Irradiation (Rayonet, 350 nm) of DCN in the presence of this borate gives four isomeric products. These were identified as 3- and 4-(5-hexenyl)-1-cyanonaphthalenes and 3- and 4-(cyclopentylmethyl)-1-cyanonaphthalenes[6] (Table 1). When this same system is irradiated with a nitrogen laser (much higher power and concentration of intermediates), the ratio of rearranged to unrearranged products decreases. Similarly, saturation of the solution with air before irradiation also causes this ratio to decrease (as well as the overall yield). Control experiments showed that these alkylated cyanonaphthalenes were not interconverted under the reaction conditions and that cyclopentylmethyltriphenylborate was not formed from the open-chain isomer. These observations clearly support carbon-boron bond cleavage[7] to form free alkyl radicals and operation of the S_n1-like mechanism outlined in Eq. 6.

$$\mathrm{DCN}^{\overline{\cdot}} + \left[\mathrm{R{-}B(Ph)_3}\right]^{\cdot} \longrightarrow \left[\mathrm{RDCN}\right]^{-} + \mathrm{B(Ph)_3} \qquad (5)$$

$$\left[\mathrm{R{-}B(Ph)_3}\right]^{\cdot} + \longrightarrow \mathrm{R}\cdot + \mathrm{B(Ph)_3} \xrightarrow{\mathrm{DCN}^{\overline{\cdot}}} \left[\mathrm{RDCN}\right]^{-} \qquad (6)$$

At first glance it seem difficult to accomodate free radical formation, high product yields, and the absence of radical dimerization products (particularly bibenzyl when $R=PhCH_2$). However, if carbon-boron bond cleavage is relatively slow, as it is for some catechol boranyl radicals,[8] then the concentration of $DCN^{\overline{\cdot}}$ in solution may build up to much higher levels than that of the alkyl radical. With the further assumption that coupling of the radical is equally fast for combination with $DCN^{\overline{\cdot}}$ and for dimerization, this difference in concentration can be readily translated into the observed product yields. We are presently attempting to measure the rate of carbon-boron bond cleavage directly.

In summary, tandem electron transfer and the isomerization of the hexenyl radical implicate a free radical mechanism for the photoalkylation of DCN by borates 1. This process seems to parallel remarkably the thermal reaction of Grignard reagents with electron-poor arenes.[9] We are exploring other examples of the photoreaction of borates that also appear to mimic the Grignard reaction.

References and Notes

1) J. Y. Lan and G. B. Schuster, J. Am. Chem. Soc., **107**, 6710 (1985).

2) The Stern-Volmer quenching constant (K_{sv}) is 132.

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5) Tetramethylammonium 5-hexenyl(triphenyl)borate: ^{1}H-NMR (300 MHz, CD_3CN) δ 7.32(bs, 6H), 6.98(t, 6H), 6.85(t, 3H), 5.80(m, 1H), 4.90(dd, 2H, J_1=7 Hz, J_2=12 Hz), 2.93(s, 12H), 2.10(m, 2H), 1.28(m, 2H), 0.95(m, 4H). Anal. Calcd. for $C_{28}H_{38}NB$: C, 84.2; H, 9.5; N, 3.5; B, 2.8. Found: C, 83.7; H, 9.7; N, 3.4; B, 2.9.

   Tetramethylammonium cyclopentylmethyl(triphenyl)borate: ^{1}H-NMR (300 MHz, CD_3CN) δ 7.35(bs, 6H), 7.00(t, 6H), 6.81(t, 3H), 3.05(s, 12H), 1.1-1.5(m, 9H), 0.81(m, 2H). Anal. Calcd for $C_{28}H_{38}NB$: C, 84.2; H, 9.5; N, 3.5; B, 2.8. Found: C, 83.8; H, 9.8; N, 3.5; B, 3.2.

6) All four isomers have exact mass calculated for $C_{17}H_{17}N$. The structural assignments were made by analysis of the ^{1}H-NMR spectra of these compounds in comparison with authentic samples of the 3- and 4-(cyclopentyl)methyl-1-cyanonaphthalenes prepared from the cyclopentylmethyl(triphenyl)borate[5] and 1,4-dicyanonaphthalene.

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