Experimental Section

Spectra were measured by use of an AEl ES 200 electron spectrometer using Al Kα as the exciting radiation. The vacuum in the sample chamber was approximately 10^{-7} Torr and there was no evidence for any O 1s signal which is coincident with the Sb 3d region. The binding energies were measured with respect to C 1s contaminant signal taken as 285 eV. In all cases the C 1s spectrum was a singlet and repeated determinations of binding energies were consistent to 0.3 eV. FWHM are accurate to ±0.2 eV. Materials were prepared by literature methods and their antimony analyses agreed with the formula given.

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Registry No. Na_2SbF_5, 36732- 24-8; K_2SbF_5, 20645-41-4; KSb_2F_7, 11088-88-3; $Co(NH_3)_6SbCl_6$, 17805-63-9; $Cs_3Sb_2Cl_9$, 12016-49-8; $Co(NH_3)_6SbBr_6$, 36527-01-2; $Cs_3Sb_2Br_9$, 12011-43-7; $Rb_3Sb_2Br_9$, 12234-36-5; $Rb_3Sb_2I_9$, 12532-41-1; $CsSbCl_6$, 19578-48-4; ^{121}Sb, 14265-72-6.

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Photolytic and Electrolytic Reduction of Iodobenzenenonahydro-*closo*-decaborate(1−) Ion, an Anionic Analog of Diphenyliodonium Ion, and Preparation of 1-Iodononahydro-*closo*-decaborate(2−) Ion

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In its formula, structure, and susceptibility to substitution reactions, the decahydro-*closo*-decaborate ion, $B_{10}H_{10}^{2-}$, has many similarities to benzene, C_6H_6. Thus, derivatives of the general type $B_{10}H_9X^{2-}$ are known, analogous to C_6H_5X compounds, where X can be any of a host of functional groups.[1] The iodobenzene derivative $B_{10}H_9IC_6H_5^-$, obtained by the reaction of $B_{10}H_{10}^{2-}$ with C_6H_5IO,[2] is an analog of the diphenyliodonium ion $(C_6H_5)_2I^+$, with the formal 2− charge of the boron cage conferring an overall negative charge on the formally positive iodine derivative. The cesium salt $CsB_{10}H_9IC_6H_5$ is reported to have a uv absorption maximum at 296 nm in acetonitrile.[2] Uv irradiation of diphenyliodonium iodide in chloroform has been reported to yield iodobenzene and benzene.[3] The $B_{10}H_9IC_6H_5^-$ ion was subjected to uv irradiation to see if a similar reaction would occur and if so, whether the boron-iodine or carbon-iodine bond would be broken.

Results

When 6 m*M* solutions of $CsB_{10}H_9IC_6H_5$ in water were irradiated with a medium-pressure mercury lamp fitted with a Corex filter (290-nm cutoff) for 4-5 hr, high-yield conversions according to eq 1 were achieved. The odor of biphenyl,

$$B_{10}H_9IC_6H_5^- + H_2O \xrightarrow{h\nu} B_{10}H_9I^{2-} + H^+ + {}^1/_2O_2 + C_6H_6 \qquad (1)$$

$C_6H_5C_6H_5$, could be detected when ether extracts of the reaction mixture were allowed to evaporate, but no isolable quantities of biphenyl were obtained. Phenol was not detected. When $CsB_{10}H_9IC_6H_5$ was irradiated in a mixture of water and 2-propanol, the reaction proceeded according to eq 2.

$$B_{10}H_9IC_6H_5^- + (CH_3)_2CHOH \xrightarrow{h\nu} B_{10}H_9I^{2-} + H^+ + (CH_3)_2CO + C_6H_6 \qquad (2)$$

The product $B_{10}H_9I^{2-}$ ion had no uv absorption maximum above 210 nm. Moderately strong ir absorptions at 1465, 1440, and 985 cm^{-1} of the starting material were not present in the product, but an absorption at 1000 cm^{-1} remained. The 32-MHz ^{11}B nmr spectrum consisted of a doublet of area 0.92 at 19.6 ppm (J_{BH} = 136 Hz), a singlet of area 0.92 at 27.1 ppm, and an apparent triplet due to two overlapping doublets of area 8.16 at 43.8 and 47.8 ppm (J_{BH} = 126 Hz), with chemical shifts upfield from external $B(OCH_3)_3$.

The $B_{10}H_9IC_6H_5^-$ ion was reduced at a dropping mercury electrode in acetonitrile at about −1.0 V (relative to sce), but not in a reversible, diffusion-controlled process. There was a pronounced maximum in the wave, the limiting current was much larger than expected, and the current-time curves for individual drops were somewhat irregular. In water, no wave was observed, but rather, there was a gradual increase in cathodic current with negative potential. Electrolysis at a mercury pool electrode at −1.2 V in acetonitrile or −1.5 V in acetonitrile-water yielded $B_{10}H_9I^{2-}$ ion and benzene. Coulometry gave *n* values of 1.3 ± 0.1 in acetonitrile and 1.8 ± 0.2 in acetonitrile-water.

Discussion

The synthesis of the $B_{10}H_9IC_6H_5^-$ ion results in apical substitution only,[2] and the ^{11}B nmr spectra confirm that this substitution geometry is retained in the product $B_{10}H_9I^{2-}$ ion. These reactions offer convenient routes to quite pure 1-$B_{10}H_9I^{2-}$ ion uncontaminated with the 2 isomer or with polyiodinated derivatives that are formed in the direct iodination of $B_{10}H_{10}^{2-}$.[4]

Although the experiments were designed and carried out primarily for purposes of product preparation rather than for mechanistic studies, some deductions concerning the course of the photoreduction can be made. The identification of $B_{10}H_9I^{2-}$ and C_6H_6 as the major products of the photolysis demonstrates that the carbon-iodine bond cleavage does *not* occur from the excited state directly. Homolytic cleavage would give a phenyl radical and a $B_{10}H_9I^{\cdot-}$ radical ion, which would dimerize to form the $B_{20}H_{17}I_2^{3-}$ ion and H^+.[5] Heterolytic cleavage to form the $B_{10}H_9I^{2-}$ ion directly would also form a phenyl cation which would react with water to give phenol. Formation of benzene could be explained by heterolytic cleavage to form a phenyl anion, but this would also generate neutral $B_{10}H_9I$, an unreasonably high-energy species analogous to a doubly ionized iodobenzene cation $C_6H_5I^{2+}$. Thus it can be concluded that reduction of the excited state precedes bond cleavage.

The photolysis of diphenyliodonium iodide in chloroform[3] yields iodobenzene, benzene, and iodine in amounts that are consistent with the results of a more detailed study of the photolysis of triphenylsulfonium iodide in chloroform, in which irradiation was carried out at the wavelength of the charge-transfer absorption.[6] The charge-transfer excited

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state $(C_6H_5)_3S{\cdot}I{\cdot}$ decomposes by a nondiffusive pathway to diphenyl sulfide and iodobenzene and by a diffusive pathway to diphenyl sulfide and phenyl radicals which form benzene by reaction with solvent. Electroreduction of diphenyliodonium ion at a mercury electrode in water[7] proceeds by an initial one-electron reduction to form diphenyliodine radicals (eq 3). Diphenyliodine radicals can then decompose to give iodobenzene and phenyl radicals (eq 4), or they can be reduced in an irreversible process to iodobenzene and benzene at a more negative potential (eq 5). Yields of iodobenzene

$$(C_6H_5)_2I^+ + e^- \rightleftarrows (C_6H_5)_2I\cdot \tag{3}$$

$$(C_6H_5)_2I\cdot \rightarrow C_6H_5I + C_6H_5\cdot \tag{4}$$

$$(C_6H_5)_2I\cdot + H^+ + e^- \rightarrow C_6H_5I + C_6H_6 \tag{5}$$

and benzene[3] suggest that the photolysis of diphenyliodonium iodide also occurs by the formation of a charge-transfer radical pair $(C_6H_5)_2I{\cdot}I{\cdot}$ which decomposes by both diffusive (eq 4) and nondiffusive pathways.

The observed electroreduction at about −1.0 V (relative to sce) and the photoexcitation energy of about 4.2 V (296 nm) of $B_{10}H_9IC_6H_5^-$ ion suggest that the excited state should be capable of oxidizing water (potential required ~+0.6 to +1.0 V), even allowing for considerable reorganization energy and changes in solvation energy. Decomposition of the one-electron reduction species $B_{10}H_9IC_6H_5{\cdot}^{2-}$ could take place either directly to $B_{10}H_9I^{2-}$ and a phenyl radical analogous to eq 4 or indirectly accompanied by an additional proton and electron transfer to $B_{10}H_9I^{2-} + C_6H_6$, analogous to eq 5. The observation of coulometric *n* values between 1 and 2 in acetonitrile and in water suggests that both pathways are possible in the electrolysis.

The photolysis of the $B_{10}H_9IC_6H_5^-$ produces a relatively "clean" product mixture for two apparent reasons. First, irradiation can be carried out at a wavelength at which the products are essentially transparent, so that no secondary photolysis of products occurs. Second, the irradiation produces a bound excited state capable of accepting an electron from the solvent, resulting in the formation of a reduced ion similar in properties to an excited charge-transfer complex which decomposes quite cleanly.

Experimental Section

A solution of 4.0 mmol of $CsB_{10}H_9IC_6H_5$ in 650 ml of water was irradiated with a medium-pressure mercury lamp fitted with a Corex filter (290-nm cutoff) for 4–5 hr, during which time the evolution gas was monitored with a gas buret. The reaction mixture was titrated with standardized sodium hydroxide solution to a pH of 7, and aqueous tetramethylammonium chloride was added. The resulting precipitate gave a 75% yield of white crystals of $Cs(CH_3)_4NB_{10}H_9I$ when recrystallized from an acetonitrile–water mixture. This double salt was converted to the more soluble $[(CH_3)_4N]_2B_{10}H_9I$ by ion exchange to the sodium salt and addition of tetramethylammonium chloride. *Anal.* Calcd for $[(CH_3)_4N]_2B_{10}H_9I$: B, 27.55; equiv wt 199.2. Found: B, 27.11; equiv wt (acid ion exchange) 200.

In order to be able to monitor the progress of the photolysis by ^1H nmr, 0.2 mmol of $CsB_{10}H_9IC_6H_5$ was converted to the sodium salt of $B_{10}H_9IC_6H_5^-$ by acid ion exchange and neutralization with sodium hydroxide. After evaporation of the solvent, the residue was transferred to an nmr sample tube with about 0.3 ml of water. Following addition of 0.3 ml of 2-propanol to the solution, the sample was irradiated in a Rayonet reactor fitted with 300-nm lamps for 2.5 hr. During this period, nmr spectra of the mixture were run at intervals of 0.5–1.0 hr. Integration of the nmr signals showed that benzene and acetone were formed in equivalent amounts and that the reaction was essentially complete in 2.5 hr.

About 50 ml of an acetonitrile–water mixture containing 2.0 mmol of $CsB_{10}H_9IC_6H_5$ was electrolyzed at a mercury pool electrode first at −1.5 V (relative to sce) and then at −2.2 V until 2.2 mequiv of current had passed. The addition of aqueous tetramethylammonium chloride caused the precipitation of 1.0 mmol of $Cs(CH_3)_4NB_{10}H_9I$, identified by its ir spectrum. Addition of more tetramethylammonium chloride afforded the recovery of 0.6 mmol of the starting material as $(CH_3)_4NB_{10}H_9IC_6H_5$. Concentration of the remaining solution led to the isolation of 0.1 mmol of $[(CH_3)_4N]_2B_{10}H_9I$.

Coulometry was carried out at a mercury pool electrode at −1.2 V in millimolar solutions of $CsB_{10}H_9IC_6H_5$ in acetonitrile containing 0.1 *M* tetraethylammonium perchlorate, using a Wenking potentiostat with a Hewlett-Packard voltage-to-frequency converter and electronic counter. Coulometric *n* values for two solutions were 1.2 and 1.4.

When electrolysis was carried out on a 0.04 *M* solution of $CsB_{10}H_9IC_6H_5$ in a 50:50 (by volume) mixture of acetonitrile and water, *n* values of 1.6 based on recovery of starting material and 2.0 based on isolated product yield were obtained.

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Registry No. $CsB_{10}H_9IC_6H_5$, 12551-04-1; $[(CH_3)_4N]_2B_{10}H_9I$, 39436-16-3.

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Electron Paramagnetic Resonance Spectra of Oxides of Titanium. Effective Magnetic Moments of Ti^{3+} Ions

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We have previously reported epr and magnetic susceptibility studies on several discrete phases of the titanium-oxygen system described by Ti_nO_{2n-1},[1-12] as have a number of other investigators.[13-16] Goodenough recently has reviewed the properties of several transition metal oxide systems, including the Ti-O system.[17,18]

In all of the epr studies the spectra observed at 77 K have been attributed primarily to the Ti^{3+} ($3d^1$) ion. Shannon[19]

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