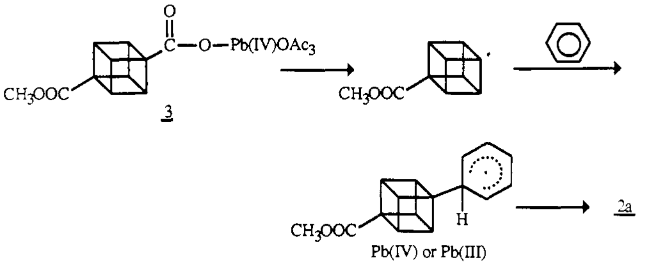
of ortho-, meta-, and para-substituted analogues, **1** → **2a** (ortho:meta:para = 36:5:58); bromobenzene, **1** → **2b** (ortho:para = 37:63); α,α,α-trifluorotoluene, **1** → **2c** (meta:para = 50:50). In the case of *o*-dichlorobenzene, a mixture of methyl 1-(*o*-dichlorophenyl)cubane-4-carboxylates is obtained.

The X-ray structure[10] of **2** is given in Figure 1. In addition to confirming the structure, the X-ray determination provides a value for the relatively short cubyl–phenyl distance, 1.482 (4) Å. In contrast, five X-ray determinations[11] of the adamantyl–phenyl distance range from 1.531 to 1.536 Å [average: 1.534 Å]. The shortened distance in **2** may be attributed to increased s character in the exocyclic cubyl orbital, which causes a cubyl–phenyl bond to more closely resemble a single bond between two sp^2 C atoms, rather than an sp^2–sp^3 bond. The cubyl–cubyl distances thus far observed have been even shorter: 1.475 (3) Å in pure cubylcubane crystals[12] and 1.458 (8) and 1.474 (5) Å in a cocrystal of two cubylcubanes.[13] This may be due to more favorable steric interactions in the perfectly staggered cubylcubane molecule; nonbonded C···C and H···H distances across the link are extremely long (3.4–3.6 Å). In **2**, there are two short C···C distances across the phenyl–cubyl link, both 3.18 (1) Å (the van der Waals C···C distance is 3.4 Å, and the distances below this limit are considered repulsive).

The mechanism of the reaction **1** → **2**, **2a**, **b** and **1** → **2c** proceeds via the cubyl radical. Thus, lead-mixed acylate **3** has been synthesized separately and shown to decompose in the appropriate aromatic solvent to yield products **2a**,**b**. Furthermore,



3 can be iodinated upon treatment with I_2 to yield methyl 4-iodocubane carboxylate[2] and also reacts with $(C_6H_5Se)_2$ to yield methyl 4-(phenylseleno)cubanecarboxylate. The reactions with I_2 and $(C_6H_5Se)_2$ are not in agreement with possible carbocationic intermediates ($R^\bullet \rightarrow Pb(IV) \rightarrow R^+ + Pb(III)$). Furthermore, arylation with $CF_3C_6H_5$ (**1** → **2c**) effectively distinguishes between the radical reaction and carbocationic processes since the CF_3 group is radical stabilizing and carbocation destabilizing as has been demonstrated in radical cyclizations.[14] Reaction **1** → **2a–d** is formally and mechanistically analogous to $Pb(OAc)_4$ arylation of apocamphane-1-carboxylic acid, for which a radical process has been established.[15]

The key reaction intermediate, namely, the cubyl radical, was found by Stock and Luh to form 4600-fold less rapidly than the *tert*-butyl radical and 3285-fold more slowly than 1-adamantyl.[4]

The observed ortho:meta:para ratios are essentially in agreement with expectation based upon polar and steric considerations. The electrophilicity of the cubyl is intermediary between sp^3 and sp^2 (electrophilicity of radicals varies in the series $p/sp^3 < sp^2 < sp$). Thus, partial rate factors for nuclear substitution of chlorobenzene by the cyclohexyl radicals, the phenyl radical, and the phenylethynyl are f_o:f_m:f_p = 5.6:3.5:2.5, 1.3:1.0:1.4, and 0.8:0.4:0.7.[16a,b] In the case of typical sp^3-centered radicals such as CH_3 or cyclohexyl, ortho substitution predominates,[17] but in the cubyl system, steric effects reverse this pattern. In the case of $CF_3C_6H_5$, the observed meta:para ratio of **1** is close to that observed with the cyclohexyl radical and $CF_3C_6H_5$ of 1.2.[16a] The relatively large amount of meta substitution in this case agrees with calculated (RHG4-31G) radical stabilization energies of substituents such as CH_3 (+3.27 kcal/mol), Cl (+2.57 kcal/mol), and CF_3 (−1.34 kcal/mol).[16c]

Acknowledgment. We thank the Office of Naval Research for support of this work under Contract FED ONR 0001486K0619. In addition, valuable discussions with Professor Harold Shechter of The Ohio State University contributed to this study.

Supplementary Material Available: Footnote 9, giving experimental details for the syntheses of **2** and **3** from **1**, footnote 10, giving X-ray data for **2**, and tables of atomic positional parameters, Cartesian coordinates, bond distances, bond angles, torsion angles, and anisotropic thermal parameters for **2** (5 pages); table of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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Microscale Glycosidic Cleavage of Oligosaccharide Bromobenzoates for Circular Dichroism Analysis

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Glycoproteins and glycolipids play important roles in biological processes.[1] Despite developments in chemical methodology,[2] ^1H NMR,[3] and GC/MS,[4] structure determinations of complex carbohydrates remain difficult because of their great number of possible isomers[5] and the microgram quantities in which many are obtained.

Approaches to determine oligosaccharide glycosidic linkages based on the CD exciton chirality method have been demonstrated.[6-8] In our recent approach, tagging free hydroxyls of an

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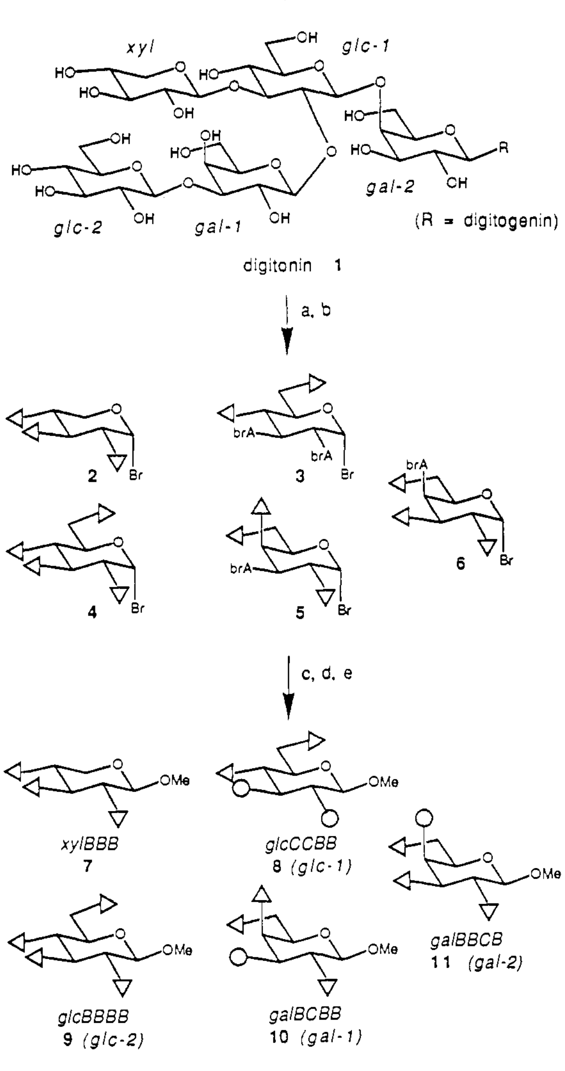
oligosaccharide with bromobenzoates (λ_{max} = 245 nm) and those involved in glycosidic linkages with methoxycinnamates (λ_{max} = 311 nm) affords "bichromophoric" sugar subunits; the identities and linkage patterns of these can be determined from their characteristic CD curves at nanomolar levels.[8] Previous efforts to cleave perbenzoylated oligosaccharides without loss or migration of acyl groups, however, were unsatisfactory.[6a] Attempts to overcome these difficulties with protection/deprotection steps were more successful yet not convenient for microscale derivatization.[6b] We report here a *modified acetobrominolysis* procedure for the direct cleavage of perbenzoylated oligosaccharides and demonstrate its application to microscale structural studies.

Acetolysis[9] and acetobrominolysis[10] conditions have been used for partial degradation of oligo- and polysaccharides. We have sought such conditions that would effect cleavage of perbenzoylated oligos without migration or deprotection, allowing for subsequent conversion of hydroxyls liberated from linkages to cinnamates for CD analysis. We have found that bromoacetyl bromide/H_2O mixtures can cleave glycosidic linkages in a variety of naturally occurring oligosaccharides with concomitant tagging of their linkage points as bromoacetate esters. Bromoacetate groups can readily be removed for subsequent derivatization of these positions.

Application of this procedure is illustrated for digitonin **1** (Figure 1).[11] Treatment of its heptadecakis(*p*-bromobenzoate) (300 μg) in $BrCH_2COBr/H_2O$ (1:1), which generates a 9.5 M $HBr/BrCH_2CO_2H$ solution, gives the α-bromoglycosides **2–6**; bromoacetylation of hydroxyls liberated from glycosidic linkages prevents migration of the bromobenzoate groups.[12] The mixture is immediately converted to stable methyl β-glycosides by using silver salts. Deprotection of bromoacetates with thiourea[13] and cinnamoylation provided the mixture of "bichromophoric" acylated glycosides **7–11**, which were separated by HPLC[14] and characterized by UV, CD, and MS; the overall yields of **7–11** from the perbenzoylated digitonin are,[15] respectively, 41%, 69%, 94%, 35%, and 31%. The four steps in this derivatization are convenient, as purification is only required after the final step to separate the subunits for spectroscopic analysis. Comparisons between CD spectra of these subunits and those of synthetically prepared samples revealed excellent agreement in all cases.[16]



△ : p-$BrC_6H_4CO_2$-; brA : $BrCH_2CO_2$-; ○ : p-$MeOC_6H_4(CH)_2CO_2$-

Figure 1. (a) p-BrBzCl/AgOTf (3 equiv/OH), DMAP (cat.), pyr, room temperature, 12 h in the dark; SiO_2 chromatography. (b) The sugar was dissolved (300 μg) in $BrCH_2COBr/H_2O$ (1:1 mol ratio), 60 μL, in a glass tube (1-mL capacity) with a Teflon spindle valve, 60 °C, 12 h; the valve was opened after cooling to −78 °C, HBr was removed in vacuo, the residue was dissolved in hexane/EtOAc (3:1), excess acid was neutralized with saturated aqueous $NaHCO_3$, the organic layer was concentrated to dryness, and the residue was lyophilized with C_6H_6 to give α-bromoglycosides **2–6**. (c) The bromo sugars **2–6** in dry $MeOH/CHCl_3$ (1:2) under Ar were converted to the β-methylglycosides in the dark with Ag_2CO_3/AgOTf (1:2 w/w), room temperature, 1 h; the mixture was concentrated to dryness, suspended in hexane/EtOAc (3:1), and filtered through a SiO_2 slurry, and the eluate was concentrated. (d) Dissolve the residue in $CHCl_3$/MeOH (2:1), add excess $NaHCO_3$ and thiourea, 2 h, room temperature; after concentration to dryness, passage of the residue suspension in hexane/EtOAc (2:3) through a SiO_2 slurry, and concentration of the eluate, lyophilization with C_6H_6 gave a white powder. (e) The powder was reacted with *p*-MeOCnCl/AgOTf/DMAP (cat.) in pyr/CH_2Cl_2 (1:4) under Ar in the dark, room temperature, 5 h, and excess acid halide was quenched with H_2O/pyr, 1 h; evaporation of the solution, passage of the residue suspension in hexane/EtOAc (3:1) through a neutral Al_2O_3 slurry, and concentration of the eluate gave the mixture **7–11**. Derivatization of the alcohol positions is represented by the order 2,3,4,6 (2,3,4 for xyl) by B = *p*-bromobenzoate and C = *p*-methoxycinnamate.

The characteristic CD curves can be used to identify unknown pyranose[17] components, including absolute configurations, and their linkage positions at nanomolar levels. Most "bichromophoric" reference spectra (totaling 144) of pyranose subunits present in glycoproteins, glycolipids, etc., including those in deoxy sugars, amino sugars and N-acetylated sugars, are now available in experimental and calculated forms.[18] We hope that the present

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(15) After preparative HPLC, respective yields were estimated from the known ε values at 245 nm (benzoate)[6b,7b] and 311 nm (cinnamate).[8a,8b]

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scheme, requiring no reference samples, will serve as a complementary method to the standard methylation analysis.[4] Current work is directed toward studies of glycoconjugates, including sequence information obtainable from partial cleavage.

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Syntheses of Divalent Lanthanide Tetradecahydrodecaborates and Decahydrodecaborates. The X-ray Crystal Structure of $(CH_3CN)_6Yb(\mu\text{-}H)_2B_{10}H_{12}\cdot 2CH_3CN$

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The chemistry and bonding of boron hydrides to the lanthanide elements remains largely unexplored. While numerous lanthanide organometallic complexes are known,[1a,b] the only boron hydride compounds reported are the trivalent *closo*-$[B_{12}H_{12}]^{2-}$ salts[2,3] and borohydride, $[BH_4]^-$, derivatives.[4,5] No detailed structural data are available; however, the gadolinium complex $(BH_4)_3Gd(THF)_3$ has been reported to be isomorphous with the pseudo-lanthanide derivative[6] $(BH_4)_3Y(THF)_3$. Compounds containing the common divalent ions (Ln = Sm, Eu, Yb) and binary boron hydride ligands are unknown; however, carborane complexes have been reported in which the metal occupies the vertex site of an icosahedron,[7] as well as a σ-bonded carborane compound.[8] Herein we report the synthesis and the first example of a structurally characterized polyhedral boron hydride bound to a lanthanide center, $(CH_3CN)_6Yb(\mu\text{-}H)_2B_{10}H_{12}\cdot 2CH_3CN$ (I). We also report the syntheses of the divalent lanthanide decahydrodecaborate compounds $EuB_{10}H_{10}$ (II) and $YbB_{10}H_{10}$ (III).

Compounds I–III are derived from reactions of decaborane(14), $B_{10}H_{14}$, with the lanthanide metals (Ln = Eu, Yb) in liquid ammonia (Scheme I). Both europium and ytterbium dissolve in NH_3 to give deep blue, highly reducing solutions containing Ln^{2+} and solvated electrons.[9] Decaborane(14) is easily reduced in these solutions, from which several products can be isolated.

The molecular structure of I, determined from a single-crystal X-ray analysis[10] (Figure 1), reveals a $B_{10}H_{14}$ unit that is coordinated to ytterbium through two B–H–Yb bridges from adjacent $BH_2(6)$ and BH(5) positions on the boron cage. All of the hydrogen atoms on the B_{10} framework were located, and their positions were refined. Their disposition in the $B_{10}H_{14}$ unit is like that in $[B_{10}H_{14}]^{2-}$, and the structural parameters are in good agreement with those of the dianion.[11] In addition, there are six roughly linear acetonitriles bound through nitrogens to the metal center. The ytterbium is formally eight coordinate, with an ir-

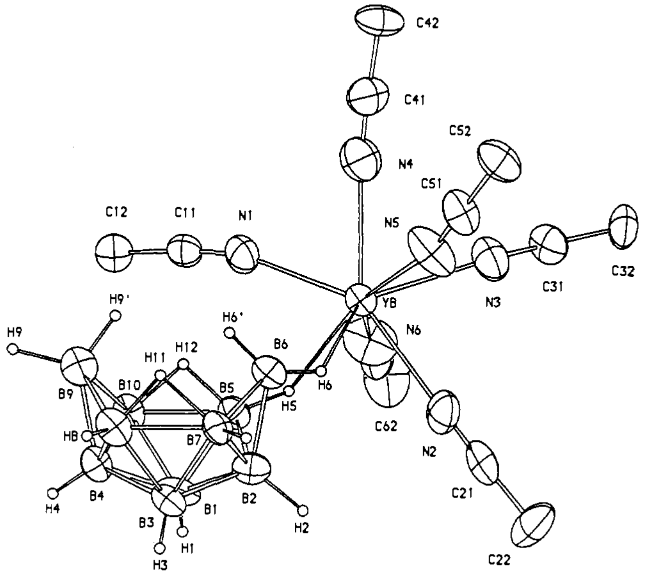
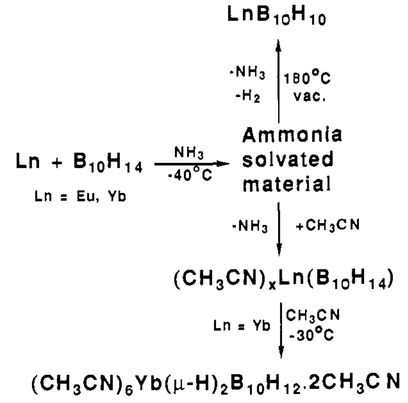
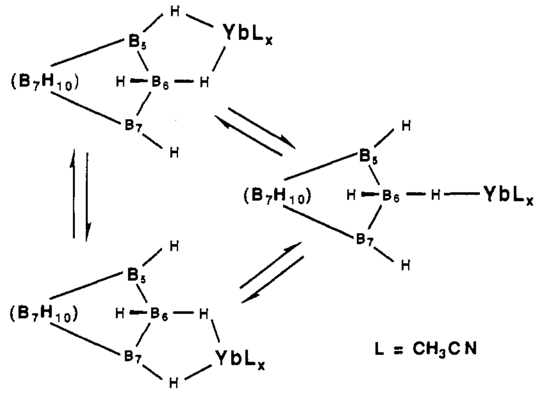


Figure 1. Molecular structure of $(CH_3CN)_6Yb(\mu\text{-}H)_2B_{10}H_{12}$ (I) (ORTEP plot with 50% probability ellipsoids). Acetonitrile hydrogens are not shown. Selected distances (Å): Yb–H(5) = 2.2 (1); Yb–H(6) = 2.4 (1); Yb–N(1) = 2.54 (1); Yb–N(2) = 2.52 (1); Yb–N(3) = 2.56 (2); Yb–N(4) = 2.53 (1); Yb–N(5) = 2.59 (2); Yb–N(6) = 2.53 (2); Yb–B(5) = 3.04 (1); Yb–B(6) = 2.83 (1). Selected bond angles (deg): H(5)–Yb–H(6) = 68 (4); B(5)–H(5)–Yb = 117 (7); B(6)–H(6)–Yb = 110 (7).

Scheme I



Scheme II



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[10] Crystal data for $(CH_3CN)_6Yb(\mu\text{-}H)_2B_{10}H_{12}\cdot 2CH_3CN$ (−45 °C): space group $P\bar{1}$, a = 8.831 (6) Å, b = 11.615 (4) Å, c = 15.568 (6) Å; α = 104.08 (3)°, β = 97.67 (4)°, γ = 94.83 (3)°; V = 1523.6 Å^3, ρ(calcd) = 1.359 g cm^{-3}, MW = 623.68, Z = 2, μ = 30.786 cm^{-1}. Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation. All data were corrected for Lorentz and polarization effects. An empirical absorption correction was made. Crystallographic computations were carried out on a PDP11/44 computer using the SDP (Structure Determination Package). The structure was solved by the direct method MULTAN 11/82 and difference Fourier synthesis. Full-matrix least-squares refinements were employed. $R_F = 0.052$, $R_{wF} = 0.063$, GOF = 1.88 (356 variables refined) for 2796 unique observations $[I \geq 3.0\sigma(I)]$ of 4145 reflections collected over the 2θ range $4° \leq 2\theta \leq 45°$. All non-hydrogen atoms were refined anisotropically except one acetonitrile of crystallization which was disordered.

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