position. Conversely, decomposition and formation of black tarry material was observed in hot toluene. Similar decomposition products were observed upon treating $CrCl_2(THF)_2$ with 2 equiv of MeLi in the presence of TMEDA. The formation of **2** can be reversed and complex **1** can be reformed just by dissolving **2** in THF, evaporating the solvent to dryness, and recrystallizing the residual solid from ether. Complex **2** is paramagnetic with a magnetic moment consistent with a monomeric square-planar d^4 Cr(II) complex (μ_{eff} = 4.98 μ_B).

The monomeric structure of **2** has been demonstrated by X-ray analysis.[9] The molecule is composed of a square-planar central monomeric Me_4Cr core [C(7)-Cr(1)-C(7a) = 180.0 (1)°, C(7)-Cr(1)-C(8) = 93.8 (2)°] connected to each of the two LiTMEDA fragments through two bridging methyl groups (Figure 1). The two identical $CrLiMe_2$ moieties are folded in a butterfly conformation with the lithium atom elevated above the Me_4Cr plane [C(7)-Cr(1)-Li(1)-Cr(8) = 131.3 (3)°]. The angles subtended at the bridging carbon atoms [Cr(1)-C(7)-Li(1) = 72.4 (2)°, Cr(1)-C(8)-Li(1) = 72.6 (2)°] are considerably narrow and, together with the short Cr-Li distances [Cr(1)-Li(1) = 2.589 (6) Å], might suggest some extent of Cr→Li bonding interaction. The Cr-C distances are elongated [Cr(1)-C(7) = 2.204 (5) Å, Cr(1)-C(8) = 2.213 (4) Å] with respect to other neutral Cr(II) alkyls[10] and are comparable to those found in complex **1** and other bridged Cr(II) aryls.[11] The lithium atoms possess a normal tetrahedral geometry with the coordination tetrahedron defined by two carbon and two TMEDA nitrogen atoms [Li(1)-C(7) = 2.176 (7) Å, Li(1)-N(1) = 2.136 (6) Å].

The cleavage of the Cr-Cr quadruple bond, obtained by replacing a Lewis base coordinated to the alkali cation, without altering the coordination environment of the transition metal, is surprising. It demonstrates that (i) the role of the alkali cation is vital to the stability of the Cr-Cr interaction of complex **1** and (ii) the Cr-Cr interaction (if any) cannot hold together the dinuclear frame in the absence of Cr-Me-Li-Me-Cr bridges. Therefore, the question again arises as to whether or not the definition of chemical bond is appropriate for the Cr-Cr interaction[12] in complex **1**, in spite of the very short intermetallic distance and the efficient magnetic coupling. Interestingly, we have found that the isostructural $Me_8Mo_2Li_4(THF)_4$[13] cannot be cleaved in similar or harder reaction conditions, in agreement with theoretical calculations which predict the existence of a significant Mo-Mo quadruple bond.[14] Another fascinating question arises from the nature of bonding in the Cr-Me-Li-Me-Cr bridges, thus expected to be responsible for holding together the dinuclear frame of **1**.[1] Although indication of the nature of this interaction cannot be provided by the poor quality structure of **1**, it might be suggested by the bonding mode of lithium with the Me_4Cr moiety of **2**. The data set of **2** was of sufficient quality to locate and refine the hydrogen atoms. The hydrogens of each bridging methyl group define a slightly distorted tetrahedron centered on carbon with the fourth position occupied by chromium. Each lithium atom is placed side-on and perpendicularly with respect to one of the three C-H bonds of each of two bridging methyl groups [Li(1)-H(7)-C(8) = 88.67°, Li(1)-H(10)-C(7) = 82.27°], forming considerably short Li···H distances [Li(1)-H(10) = 2.064 Å, Li(1)-H(7) = 1.992 Å]. These geometrical features suggest, as long as we consider the hydrogen atom positions as significant, that the sp^3 orbital of the bridging carbon atom is oriented mainly toward the transition metal. Thus, the short Cr-Li distance of **2**, the folding of the Me_2CrLi core, and the narrow angle subtended at the carbon atom might be regarded as the optimal distance imposed by the two Li-H agostic interactions, rather than as an improbably strong Cr→Li bond.

We are currently exploring the chemical reactivity and the possible catalytic features of complex **2**.

Acknowledgment. This work was supported by the Natural Sciences and Engineering Research Council of Canada (operating grant) and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: Tables listing atomic positional parameters, anisotropic thermal parameters, and complete bond distances and angles for **2** (14 pages); listing of observed and calculated structure factors for **2** (10 pages). Ordering information is given on any current masthead page.

(9) Crystal data for **2**: orthorhombic, *Pcab*, a = 12.707 (5) Å, b = 15.600 (6) Å, c = 11.829 (6) Å, V = 2345 (3) Å^3, Z = 4, R = 0.049 (R_w = 0.047) for 191 parameters and 1411 significant reflections out of 2382 collected at T = 100 K. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in difference Fourier maps and refined isotropically in the last cycle of full-matrix refinement.

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Determination of Absolute Stereochemistry of Acyclic 1,3-Polyols by a Difference CD Method

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Determination of the absolute configuration of acyclic 1,3-polyols by a spectroscopic method remains a difficult task. Over 200 1,3-polyhydroxylated polyene macrolides are known,[1] but the stereochemistry is established in only a handful of cases.[2-7] In these stereochemical studies, ^{1}H NMR analysis has been used for the assignment of relative stereochemistry. Recently, ^{13}C NMR analysis of 1,3-diol acetonides has proved to be a simple and reliable method for determining the relative configurations of *syn*- and *anti*-1,3-diols.[8,9] On the other hand, the CD exciton chirality method has played an important role in determining the absolute configuration of rigid molecules.[10] However, the method is rarely applied to acyclic polyols because regioselective introduction of chromophores to the polyols is difficult and the conformation of an acyclic system is more complex than that of a cyclic system. Application of the method to acyclic 1,2-polyols has been extensively studied by Nakanishi,[11] but the extension to skipped

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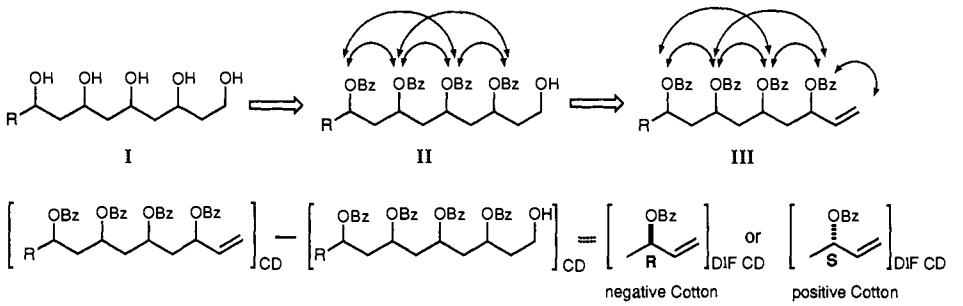
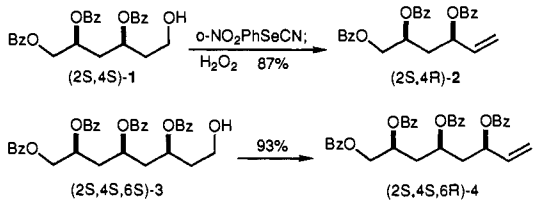


Figure 1. Major interactions of chromophores in **II** and **III** (indicated by arrows) and correlations of the DIF CD Cotton effects to the absolute configurations of the allylic position.

Scheme I



polyols was limited to only simple 1,3-diols.[12] The recent progress of new synthetic methods for 1,3-polyols[13] has also stimulated the development of new methods for determining their absolute stereochemistry. We report here an advancement in this area in which the difference CD (DIF CD) method is introduced to solve the above problems (Figure 1).

Regioselective introduction of chromophores to **I** should be difficult, but the terminal primary hydroxyl may be differentiated from the secondary hydroxyl centers. Selective protection of the primary hydroxyl, such as tritylation, followed by perbenzoylation and deprotection could afford hydroxy benzoate **II**, the dehydration of which would give allylic benzoate **III**. The CD Cotton effect of **III** reflects the overall interactions of the exciton chiralities between four benzoates and one double bond. The terminal allylic system exhibits the first Cotton effect of the benzoate transition at 230 nm which is affected by the allowed $\pi \rightarrow \pi^*$ transition of a double bond at 195 nm.[14] In addition, the sign of the first Cotton effect is diagnostic of the absolute configuration of an allylic position.[15] However, the overlapping of the additional exciton-split CD Cotton effects of benzoate chromophores around 230 nm makes it difficult to evaluate the sign and magnitude of the Cotton effect of the allylic system. The interchromophoric transitions of benzoates can be estimated from the CD spectrum of hydroxy benzoate **II**. Since **II** and **III** have the same structure except for their terminal functional groups, both are considered to adopt approximately the same conformation, including the population of possible rotamers. Therefore, subtraction of the CD curve of **II** from that of **III** would be expected to give a DIF CD curve attributable to the allylic benzoate system in **III**.

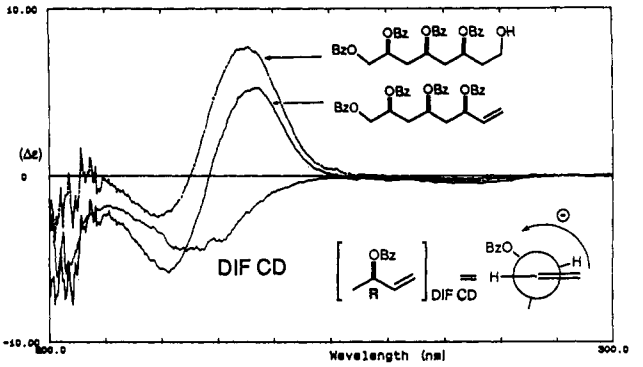
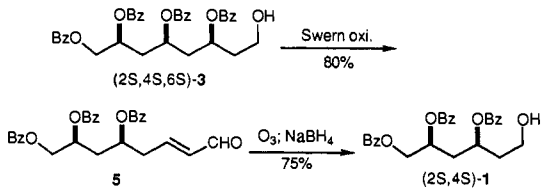


Figure 2. CD spectra of (2*S*,4*S*,6*S*)-**3** and (2*S*,4*S*,6*R*)-**4** and the difference CD spectrum.

Table I. Difference CD Data between Allylic Benzoates and Hydroxy Benzoates

entry	allylic benzoate	hydroxy benzoate	DIF CD, nm ($\Delta\epsilon$)	abs config of allylic position
1	(2*S*,4*R*)-**2**	(2*S*,4*S*)-**1**	222.2 (−4.40)	*R*
2	(2*S*,4*S*)-**2**	(2*S*,4*R*)-**1**	232.0 (+3.04)	*S*
3	(2*R*,4*R*)-**2**	(2*R*,4*S*)-**1**	232.0 (−3.04)	*R*
4	(2*R*,4*S*)-**2**	(2*R*,4*R*)-**1**	223.1 (+4.36)	*S*
5	(2*S*,4*S*,6*R*)-**4**	(2*S*,4*S*,6*S*)-**3**	224.4 (−4.88)	*R*
6	(2*S*,4*R*,6*R*)-**4**	(2*S*,4*R*,6*S*)-**3**	235.4 (−2.33)	*R*
7	(2*S*,4*R*,6*S*)-**4**	(2*S*,4*R*,6*R*)-**3**	225.8 (+4.57)	*S*
8	(2*S*,4*S*,6*R*)-**4**	(2*S*,4*S*,6*R*)-**3**	232.8 (+2.90)	*S*

Scheme II



In order to evaluate this idea, eight pairs of hydroxy benzoates and the corresponding allylic benzoates were prepared as a model system.[13d,e,16] The CD spectra of (2*S*,4*S*,6*R*)-**4** and (2*S*,4*S*,6*S*)-**3** and the corresponding DIF CD spectrum are shown in Figure 2. The DIF CD data for various pairs of stereoisomers are summarized in Table I.[17] It should be noted that the *R* and *S* designations for the configurations of each pair may vary with the right terminal substituent. In all cases studied, the DIF CD curves were nicely extracted from the CD spectra of allylic

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(17) CD and DIF CD spectra were recorded from 300 to 200 nm on a JASCO J-600 spectropolarimeter driven by a J-600 data processor. Methanol solutions were prepared which were 30–50 μM; the exact concentrations were determined from the UV extinction coefficients: tribenzoates, ϵ_{229nm} = 36 400, tetrabenzoates, ϵ_{229nm} = 48 000.

benzoates, and the signs of the Cotton effects were characteristic of the chirality of allylic positions, irrespective of the number and the stereochemistry of benzoates in the chain. The magnitude of the DIF CD also indicated that allylic benzoates having a benzoyl 1,3-*syn* to an allylic benzoyl showed a value of $|\Delta\epsilon| > 3.5$ (entries 1, 4, 5, and 7), whereas those having a 1,3-*anti* relationship showed $|\Delta\epsilon| < 3.5$ (entries 2, 3, 6, and 8).[18]

The combination of this DIF CD method with reiterative degradation enabled us to determine the absolute stereochemistry of 1,3-polyols. Thus, the Swern oxidation[19] of (2*S*,4*S*,6*S*)-**3** yielded the unsaturated aldehyde **5**, and its ozonolysis afforded hydroxy benzoate (2*S*,4*S*)-**1** (Scheme II). Dehydration of an aliquot sample of (2*S*,4*S*)-**1** gave allylic benzoate (2*S*,4*R*)-**2**, and the DIF CD measurement at this stage established the absolute configuration of the C-4 allylic position (entry 1). This series can be repeated until the stereochemistry of all chiral centers has been determined.

In summary, the difference CD method presented here has solved complicated conformational problems in acyclic 1,3-polyols. By combinating this method with reiterative degradation, the absolute stereochemistry of 1,3-polyols can be determined, even if the relative stereochemistry is unknown.

Acknowledgment. This research was supported by a grant from the Naito Foundation.

Supplementary Material Available: CD and DIF CD spectra of compounds **1-4** listed in Table I (2 pages). Ordering information is given on any current masthead page.

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Efficient Photosensitized Pyrimidine Dimer Splitting by a Reduced Flavin Requires the Deprotonated Flavin

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Pyrimidine dimers in DNA are split by photolyases, novel repair enzymes that bind to dimer-containing DNA in a dark reaction and subsequently split the dimer in a light-dependent step.[1] All known photolyases employ a reduced flavin cofactor ($FADH_2$) and either a deazaflavin or a reduced folate, which apparently function as antennas for the more efficient capture of light by the enzyme.[2] Dimer splitting appears to be a consequence of photoinduced electron transfer to or from the dimer.[3] Although a reduced flavin would be expected to be a source of electrons,[2d,4] the direction of electron transfer in the natural system is unknown.[5] We report herein the finding that, in aqueous solution, a reduced flavin requires deprotonation to the monoanion for efficient photosensitization of *N*(1),*N*(3)-dimethyluracil *cis-syn*-cyclobutane dimer[6] (DMUD) splitting (Figure 1). We also found that dimer splitting occurred by an unprecedented chain reaction, which amplified the splitting efficiency and made possible the determination of the reaction's pH profile. The results strongly imply that in this system, and possibly also the natural system, photoinduced electron transfer occurs *from* deprotonated, reduced flavin *to* dimer, with subsequent splitting by the dimer radical anion.[7]

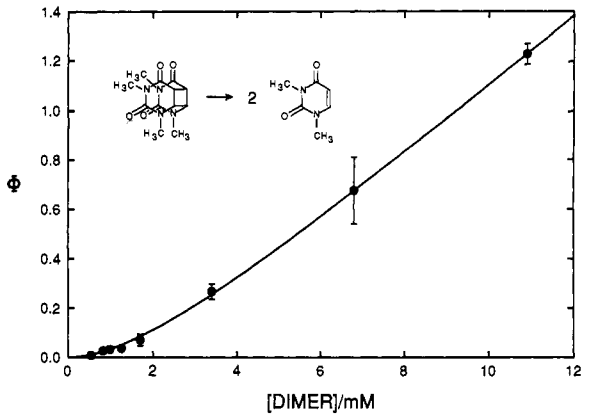

Figure 1. Dependence of DMUD splitting efficiency on dimer concentration at pH 6.3 in argon-purged (Oxiclear filter for trace O_2 removal) aqueous solution. The concentration of ac_4rfH_2 was 7.5 μM. Points are averages of at least two determinations ±SD. The line through the data was generated by curve-fitting an expression [of algebraic form $y = x^2/(ax + b)$] derived for the chain mechanism described in the text.

For these studies 2′,3′,4′,5′-tetraacetylriboflavin[8] (ac_4rf) was reduced to the 1,5-dihydroflavin (ac_4rfH_2) by irradiation at 436 nm in aqueous solutions of oxalate under an argon atmosphere.[9] Reduction appeared to be complete within approximately 30 s, whereupon UV-visible absorption spectroscopy showed the disappearance of maxima at 375 and 445 nm, which are characteristic of oxidized flavins. Irradiation in the presence of DMUD at different concentrations was carried out for a total of 10 min, after which air was admitted, the flavin was returned to the oxidized form, and a final absorbance measurement was made. The quantum yield of splitting (Figure 1) was determined on the basis of the increase in absorbance that accompanies the appearance of dimethyluracil (DMU). Following a prolonged photolysis (110 min), NMR spectroscopy verified the formation of DMU, as did HPLC after short photolyses. A control experiment was carried out with the oxidized flavin, which proved to be ineffective at dimer splitting under these conditions (data not shown).

A sensitization plot (Φ_{spl}^{-1} vs $[dimer]^{-1}$) is decidedly curved (not shown), in contrast to what is typically observed for photosensitized dimer splitting.[3g] This finding, along with the high quantum yields of splitting and quadratic dependence on [DMUD] (Figure 1), suggested the involvement of a chain reaction. A mechanism consistent with these results is electron transfer from the photoexcited flavin (ac_4rfH^{-*}) to DMUD, followed by splitting[10] of

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(10) The dimer and pyrimidine radical anions may be protonated to form their conjugate acids (i.e., the corresponding neutral radicals) in these solutions, which may affect the chain propagation steps (electron transfer and dimer radical splitting).

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