methyl groups. However, it follows from Figure 1 that the $^{13}$C assignment of the two methyl carbons was incorrect in earlier work. The resonance assignments of many other protonated and nonprotonated carbon resonances follow in a straightforward manner from such a long-range $^1H$-$^{13}C$ shift correlation spectrum. By use of this method in combination with other recently developed techniques, complete and unambiguous $^1H$ and $^{13}C$ assignments have been made. In a forthcoming publication, this reassignment will be reported, together with confirmational information derived from 2D NOE data.

The spectrum of coenzyme B$_{12}$ clearly demonstrates that with the new method determination of long-range $^1H$-$^{13}C$ connectivity is now feasible for relatively large molecules, using small sample quantities. In addition, the ability to suppress direct connectivity is helpful for minimizing the complexity of the long-range CH connectivity map. If more than one long-range CH connectivity is detected for one particular proton, the relative intensities of the corresponding resonances are directly related to the magnitude of the coupling constant. For example, the presence of an intense correlation between proton C8 and carbon C42 indicates that this coupling is significantly larger than the coupling between proton C8 and carbon C36, for which no connectivity is observed. This information may be used for distinguishing gauche (small coupling) and trans (larger coupling) conformations. In combination with other 2D experiments, the long-range multiple quantum method provides a direct method for determining both the structure and the complete and unambiguous $^1H$ and $^{13}C$ assignments of molecules of up to at least 1600 daltons.

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Synthesis of Alternating Hydroxy- and Methyl-Substituted Hydrocarbons by Oxymercuration of Cyclopolypropinol

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In addition to the Corey, Woodward, and Stork ring-disconnection methods used for the formation of poly-


(13) Cryomagnet Systems Inc., Indianapolis, IN 46203.

(14) Hansen, P. E. Prog. Nucl. Magn. Reson. Spectrosc. 1981, 14, 175 (15) For the structure of coenzyme B$_{12}$ and the IUPAC numbering system, see ref. 17.

propionate-derived natural products, the aldol condensation,16 hydroboration of allylic alcohols,14 reduction of β-hydroxy ketones,15 cuprate-mediated opening of epoxy alcohols,16 and hetero-Diels–Alder reaction15b have been used to synthesize alternating hydroxy- and methyl-substituted hydrocarbons.2 These methods have been extremely effective in acyclic systems but are of limited utility in the synthesis of cyclic 2-methyl 1,3-diols.

The observation of oxygen-directed cyclopropanation of acyclic3a and cyclic4 allylic alcohols and previous work on the stereo-specific oxymercuration of cyclopropanes4 prompted us to study the reaction of cyclopropylcarbinols with mercury(II) salts (eq 1 and 2).


Potential problems such as epoxide formation and solvolysis in the oxymercuration of conformationally flexible cyclopropylcarbinols do not interfere with this transformation. Oxymercuration of acyclic cyclopropanes 6–9 followed by reduction provided diols 15–18. Although both mercuric nitrate and acetate can be used (45:1 and 57:1 inversion/retention of configuration at carbon, respectively) for the oxymercuration of cyclopropane 9, the high solubility of mercuric trifluoracetate in organic solvents makes it the reagent of choice. The polar solvents required to dissolve mercuric acetate and nitrate apparently compete with the cyclopropane in ligating the mercuric salt, which leads to exceedingly long reaction times.

Treatment of free alcohol 10a and its corresponding tert-butyldiphenylsilyl ether 10b with mercuric salts led to complex product mixtures. Reaction of acetate 10c with mercuric trifluoracetate provided diol 19 after reduction, presumably by internal participation of the carbonyl oxygen of the acetate via a favorable six-membered ring intermediate. The homocyclopropyl oxygen, which is necessary for further elaboration of the acyclic chain, surprisingly results in a decrease in stereoselectivity of the oxymercuration relative to substrate 6.

The overall transformation of an allylic alcohol via the cyclopropane to its 2-methyl 1,3-diol using the strategy described above complements stereoechemically the hydroboration of secondary alcohols. The availability of optically pure allylic alcohols5 has been extended to cyclopropanediols.

(5) Typical procedure: A solution of cyclopropane 4 (0.24 mmol) and Hg(O,CCF,),(0.52 mmol) in CHCl, (2 mL) was stirred at room temperature for 12 h. Saturated NaCl (6 mL) was added and the two phases were shaken vigorously for 20 min. The aqueous phase was extracted with CHCl, (3 × 4 mL). The combined organic layers were dried (Na2SO4) and concentrated in vacuo to a viscous oil. This residue was dissolved in THF (1 mL) and added to a solution of LiAlH4 (1.6 mmol) in THF (3 mL) at 0 °C under N2. After 1 h at 0 °C the reaction was diluted with Et2O (4 mL) and quenched sequentially with (1) H2O (0.6 mL), (2) 15% NaOH (0.2 mL), and (3) H2O (0.18 mL). The resulting precipitate was stirred for 30 min, filtered, and washed with hot EtOAc. The filtrate was concentrated in vacuo and flash chromatographed (75% EtOAc/petroleum ether) to produce diol 13 (26 mg, 35% yield).

(6) Product distributions were determined by capillary gas chromatography (50-m OV-101 column) of the permethylsilyl ethers. Diols 11–19 were characterized by 1H NMR (270 MHz), 13C NMR (80 MHz), IR, and MS (Cl). The regiochemistry of diols 11–16 was elucidated by oxidation (Na2Cr2O7/H2SO4/acetone) of the 1,3-diols to the corresponding β-diketones, while the stereochemistry was determined by 13C NMR. The stereo- and regiochemistry of adducts 17 and 18 were determined by comparison with the products of dimethyl cuprate and trimethylaluminum mediated opening of the corresponding epoxy ethers.4

(7) Authentic sample of the minor diastereomer was prepared by (a) Mitsunobu inversion of the major diol or (b) oxidation followed by reduction of the major product.

Table I. The stereochemistry of the methyl-bearing carbon is determined by the cyclopropanation, and the orientation of the newly formed hydroxy group is defined by both the cyclopropanation and the oxymercuration. The inductive effect of the cyclopropyl oxygen presumably controls the regiochemistry of this transformation (>250:1 for the only substrates, 8 and 9, tested by GC analysis).

Treatment of cyclopropanes 2–4 with mercuric trifluoracetate resulted in oxymercuration with >70:1 inversion of configuration at the electrophilic carbon to form 2-methyl 1,3-diols 11–13, respectively, after reductive workup with lithium aluminum hydride.5 Regiocontrolled formation of diol 14 demonstrates that the electronic effect of the carbinol oxygen overrides the preference for diaxial opening of conformationally anchored norcarane derivative 5. Isolation of an unidentified diol (2.5% yield) from this reaction indicates diequatorial opening of cyclopropanes is an energetically unfavorable process. The requirement of entry of the oxygen nucleophile from inside the ring precludes the use of oxymercuration of cyclopropanes endocyclic to medium rings as confirmed by our inability to form 2-methyl-1,3-dihydroxy-cyclooctane from trans-2-hydroxy[cyclooctane (6)[1]bicyclooctane (1).
and cyclopentadienylcarbodioxide
togens for the synthesis of chiral 2-methyl 1,3-diol using the oxygenmetaration of the corresponding cyclopropylcarbinols. For the synthesis of the more highly oxygenated natural products the carbon mercury bond of the intermediate organomercuric can be converted into a carbon oxygen

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**Metal Vapor Synthesis of a Novel Triple-Decker Sandwich Complex:**

(\(\eta^5\)-Mesitylene)\((\mu-\eta^5:\eta^1\text{-mesitylene})\)Cr

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The reaction of transition-metal vapors with arene substrates is a well-established route to host of bis(arene)metal sandwich complexes, some of which are difficult or impossible to prepare by more conventional methods. We wish to report here preliminary evidence which indicates that under conditions of high metal loadings these reactions can lead to the formation of oligomeric byproducts formulated as multiple-decker sandwich complexes.

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