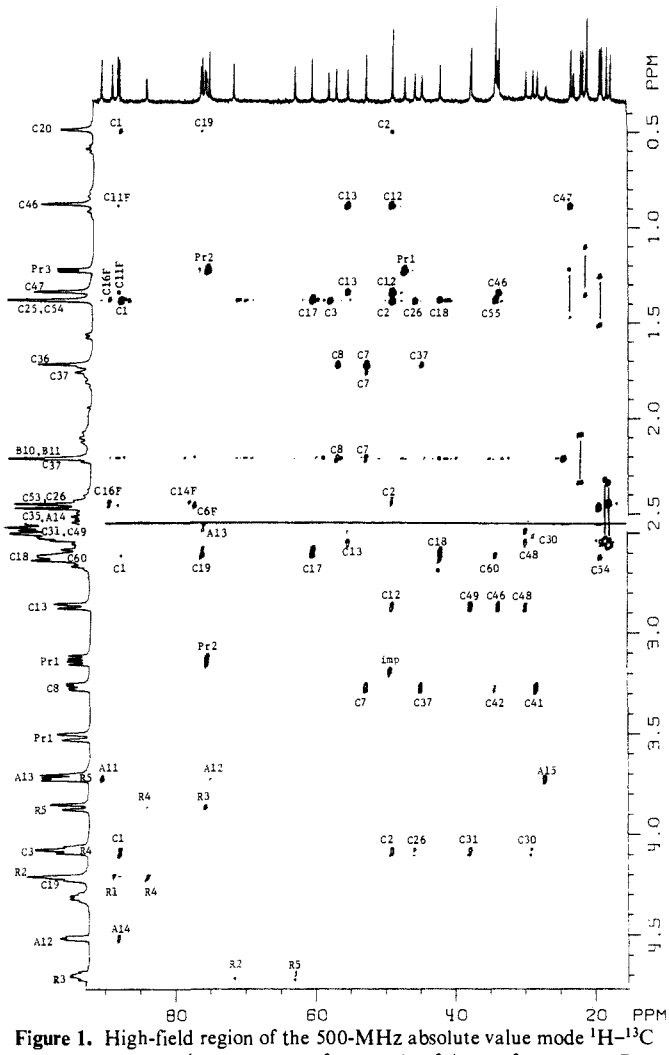

Figure 1. High-field region of the 500-MHz absolute value mode $^1H-^{13}C$ long-range correlation spectrum of a sample of 4 mg of coenzyme B_{12}, dissolved in 0.35 mL of D_2O. The measuring time was 15 h. The lowest contour level in the upper half of the spectrum (above the drawn line) has been chosen 3 times higher than for the lower half, because, at lower contour levels, t_1 noise from the intense methyl signals starts obscuring the connectivities of interest. At the top of the spectrum, the conventional ^1H-decoupled ^{13}C spectrum recorded on a JEOL GX400 spectrometer (using 50 mg of sample) is shown. Incompletely suppressed direct correlations, marked by vertical bars, are observed for the methyl groups C53, C35, B10, B11, C54, C25, C47, and Pr3.[15] Resonances that are folded in the ^{13}C dimension are labeled "F".

buffered D_2O (pH 7.0), in a 5-mm sample tube. Spectra were recorded on a modified NT-500 spectrometer, equipped with a Cryomagnet Systems ^1H probe[13] with a heteronuclear decoupling coil. The high-field part of the spectrum obtained with this method is shown in Figure 1. The entire spectrum contains well over 100 correlations. Connectivities to methyl groups are particularly intense when observed with this method since three methyl protons are used to detect the presence of a single ^{13}C nucleus. Also, both the two-bond and three-bond J_{CH} couplings to methyl protons are usually rather large (4–5 Hz[14]), sufficient to provide an efficient transfer mechanism. For example, Figure 1 shows connectivity between the protons of methyl group 46[15] and carbons C12, C47, and C13. Similarly, the C47 methyl protons show connectivity to C46, C12, and C13. This confirms that the two methyl groups C46 and C47 are attached to the same carbon, C12. A 2D NOE spectrum confirmed the original ^1H assignments[16] of the two methyl groups. However, it follows from Figure 1 that the ^{13}C assignment of the two methyl carbons was incorrect in earlier work.[17] 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,[18,19] complete and unambiguous ^1H and ^{13}C assignments have been made. In a forthcoming publication[20] this reassignment will be reported, together with conformational 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.[14] 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.

Acknowledgment. We thank Rolf Tschudin for continuous technical support and professor Luigi G. Marzilli (Emory University) for providing the sample of coenzyme B_{12}.

Registry No. (5'-Deoxyadenosyl)cobalamin, 13870-90-1.

(13) Cryomagnet Systems Inc., Indianapolis, IN 46203.
(14) Hansen, P. E. *Prog. Nucl. Magn. Reson. Spectrosc.* **1981**, *14*, 175.
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(17) Bratt, G. T.; Hogenkamp, P. C. *Biochemistry* **1984**, *23*, 5653 and references therein.
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Synthesis of Alternating Hydroxy- and Methyl-Substituted Hydrocarbons by Oxymercuration of Cyclopropylcarbinols

David B. Collum

Department of Chemistry, Cornell University
Ithaca, New York 14853

W. Clark Still and Fariborz Mohamadi*

Department of Chemistry, Columbia University
New York, New York 10027

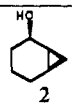
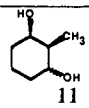
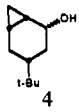
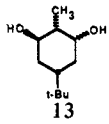
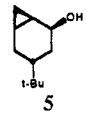
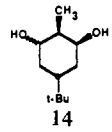
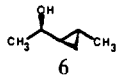
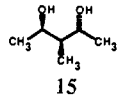
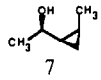
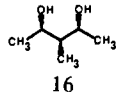
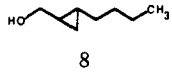
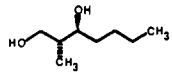
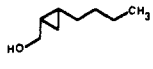
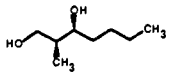
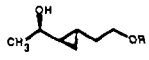
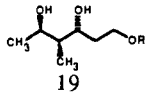
Received December 16, 1985

In addition to the Corey,[1a] Woodward,[1b] and Stork[1c] ring-disconnection methods used for the formation of poly-

(1) (a) Corey, E. J.; Trybulski, E. J.; Melvin, L. S., Jr.; Nicolaou, K. C.; Secrist, J. A.; Lett, R.; Sheldrake, P. W.; Falck, J. R.; Brunelle, D. J.; Haslanger, M. F.; Kim, S.; Yoo, S. *J. Am. Chem. Soc.* **1978**, *100*, 4619. Corey, E. J.; Trybulski, E. J.; Melvin, L. S.; Jr.; Nicolaou, K. C.; Lee, R.; Falck, J. R.; Brunelle, D. J.; Haslanger, M. F.; Kim, S.; Yoo, S. *J. Am. Chem. Soc.* **1978**, *100*, 4620. (b) Woodward, R. B.; Logusch, E.; Nambiar, K. P.; Sakan, K.; Ward, D. E.; et al. *J. Am. Chem. Soc.* **1981**, *103*, 3210, 3213, 3215. (c) Stork, G.; Paterson, I.; Lee, F. K. C. *J. Am. Chem. Soc.* **1982**, *104*, 4686. (d) Heathcock, C. H. *Science (Washington, D.C.)* **1981**, *214*, 395. Masamune, S.; Choy, W. *Aldrichimica Acta* **1982**, *15*, 47. Evans, D. A.; Nelson, J. V.; Taber, T. R. *Top. Stereochem.* **1982**, *13*, 1–115. (e) Kishi, Y. *Pure Appl. Chem.* **1981**, *53*, 1163. Still, W. C.; Barrish, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 1487. (f) Oishi, T.; Nakata, T. *Acc. Chem. Res.* **1984**, *17*, 338. Narasaka, K.; Pai, F.-C. *Tetrahedron* **1984**, *40*, 2233. Masamune, S.; Imperiali, B.; Garvey, D. S. *J. Am. Chem. Soc.* **1982**, *104*, 5528. (g) Nagaoka, H.; Kishi, Y. *Tetrahedron* **1981**, *37*, 3873. Roush, W. R.; Adam, M. A.; Peseckis, S. M. *Tetrahedron Lett.* **1983**, *24*, 1377. (h) Danishefsky, S.; Harvey, D. F. *J. Am. Chem. Soc.* **1985**, *107*, 6647.

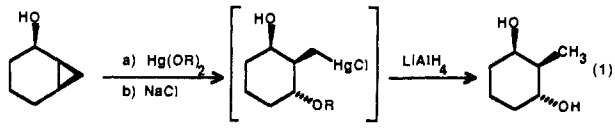
0002-7863/86/1508-2094$01.50/0

Table I[6]

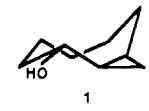
starting material	product	stereo-selectivity (inver:reten)	yield
 2	 11	73:1[7b]	62%
 3	 12	>100:1[7b]	57%
 4	 13	>80:1[7a]	58%
 5	 14		50%
 6	 15	42:1	41%
 7	 16	77:1	52%
 8	 17	45:1	69%
 9	 18	57:1	58%
 10a, R = H 10b, R = Si(Ph)$_2$(t-Bu) 10c, R = Ac	 19	19:1[7b]	40%

propionate-derived natural products, the aldol condensation,[1d] hydroboration of allylic alcohols,[1e] reduction of β-hydroxy ketones,[1f] cuprate-mediated opening of epoxy alcohols,[1g] and hetero-Diels–Alder reaction[1h] 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 acyclic[3a] and cyclic[3b] allylic alcohols and previous work on the stereospecific oxymercuration of cyclopropanes[4] prompted us to study the reaction of cyclopropylcarbinols with mercury(II) salts (eq 1 and 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 cyclopropylic 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 trifluoroacetate 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 conformationlly 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-dihydroxycyclooctane from *trans*-2-hydroxy[6.1.0]bicyclononane (**1**).



1

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 trifluoroacetate 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 trifluoroacetate produced diol **19** after reduction, presumably by internal participation of the carbonyl oxygen of the acetate via a favorable six-membered ring intermediate. The homocyclopropylic 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 stereochemically the hydroboration of secondary allylic alcohols. The availability of optically pure allylic alcohols[8]

(2) Wehrli, W. *Top. Curr. Chem.* **1977**, *72*, 21. Rinehart, K. L., Jr.; Shield, L. S. *Fortschr. Chem. Org. Naturst.* **1976**, *33*, 231. Agtarap, A.; Chamberlin, J. W.; Pinkerton, M.; Steinrauf, L. *J. Am. Chem. Soc.* **1967**, *89*, 5737. Duchamp, D. J.; Branfman, A. R.; Button, A. C.; Rinehart, K. L., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 4077.

(3) (a) Mohamadi, F.; Still, W. C. *Tetrahedron Lett.*, in press, and references cited within. (b) Simmons, H. E.; Cairns, T. L.; Vladuchick, S. A.; Hoiness, C. M. "Organic Reactions"; Wiley: New York, 1973; Vol. 20, pp 1–132. Seyferth, D.; Mai, V. A. *J. Am. Chem. Soc.* **1970**, *92*, 7412.

(4) Collum, D. B.; Mohamadi, F.; Hallock, J. S. *J. Am. Chem. Soc.* **1983**, *105*, 6882.

(5) Typical procedure: A solution of cyclopropane **4** (0.24 mmol) and $Hg(O_2CCF_3)_2$ (0.52 mmol) in CH_2Cl_2 (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 CH_2Cl_2 (3 × 4 mL). The combined organic layers were dried (Na_2SO_4) and concentrated in vacuo to provide a viscous oil. This residue was dissolved in THF (1 mL) and added to a solution of $LiAlH_4$ (1.6 mmol) in THF (3 mL) at 0 °C under N_2. After 1 h at 0 °C, the reaction was diluted with Et_2O (4 mL) and quenched sequentially with (1) H_2O (0.061 mL), (2) 15% NaOH (0.061 mL), and (3) H_2O (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, 58% yield).

(6) Product distributions were determined by capillary gas chromatography (50-m OV-101 column) of the pertrimethylsilyl ethers. Diols **11–19** were characterized by ^1H NMR (270 MHz), ^{13}C NMR (80 MHz), IR, and MS (CI). The regiochemistry of diols **11–16** was elucidated by oxidation ($Na_2Cr_2O_7/H_2SO_4$/acetone) of the 1,3-diols to the corresponding β-diketones, while the stereochemistry was determined by ^{13}C 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 alcohols.[1g]

(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.

and cyclopropylcarboxaldehydes[9] allows for the synthesis of chiral 2-methyl 1,3-diols using the oxymercuration of the corresponding cyclopropylcarbinols. For the synthesis of the more highly oxygenated natural products the carbon mercury bond of the intermediate organomercurial can be converted into a carbon oxygen bond.[10]

Acknowledgment. We thank the National Science Foundation for support (CHE 81-03030).

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(9) Abdallah, H.; Gree, R.; Carrie, R. *Tetrahedron Lett.* **1982**, *23*, 503. Arai, I.; Mori, A.; Yamamoto, H. *J. Am. Chem. Soc.* **1985**, *107*, 8254. Mash, E. A.; Nelson, K. *J. Am. Chem. Soc.* **1985**, *107*, 8256.
(10) Hill, C. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 870.

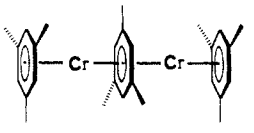
Metal Vapor Synthesis of a Novel Triple-Decker Sandwich Complex: (η^6-Mesitylene)$_2$(μ-η^6:η^6-mesitylene)Cr$_2$

William M. Lamanna

3M Central Research Laboratories
St. Paul, Minnesota 55144
Received December 4, 1985

The reaction of transition-metal vapors with arene substrates is a well-established route to a host of bis(arene)metal sandwich complexes, some of which are difficult or impossible to prepare by more conventional methods.[1,2] 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*.

Cocondensation of chromium vapor with neat mesitylene in a rotary metal atom reactor[3] produces the expected complex (η^6-mesitylene)$_2$Cr (**1**). When the reaction is conducted at high metal to ligand ratios a previously undetected byproduct formulated as the novel triple-decker sandwich complex (η^6-mesitylene)$_2$(μ-η^6:η^6-mesitylene)Cr$_2$ (**2**) is formed.[4] In pure form, the



2

bimetallic triple-decker exists as a dark, crystalline solid.[5] Despite its high molecular weight, the complex is readily soluble in ethers and aliphatic and aromatic hydrocarbons. Solutions of **2** are deep red and extremely oxygen sensitive; air exposure leads to rapid conversion to **1**, free mesitylene, and chromium oxide. The complex exhibits reasonably good thermal stability, decomposing slowly above 70 °C to a mixture of **1**, free mesitylene, and chromium metal.

Although there exist numerous examples of multiple-decker sandwich complexes containing from two to five metal atoms in a single chain,[6-15] complex **2** is the first homoleptic complex of this type containing all arene ligands. Only one other compound in this class, (η^5-C_5H_5)$_2$(μ-η^6:η^6-arene)V_2, possesses an η^6-arene ring symmetrically bridging two metal centers.[11] The (mesitylene)$_3$Cr$_2$ triple decker is formally a 30-electron complex and thus obeys the 30/34 electron rule put forth by Hoffmann et al. to account for the stability of certain triple-decker sandwiches.[16] A more recent theoretical analysis predicts the stability of structure **2** on the basis of HOMO-LUMO energy gap arguments.[17]

The proposed stoichiometry in **2** was established by elemental analysis (±0.6% for C, H, and Cr). Formulation of the triple-decker sandwich structure is based on evidence for ^{1}H and ^{13}C NMR spectroscopy. The chemical shift and coupling constant data for **2** are summarized below:[18] ^{1}H δ 3.4 (s, 6 H, Ar ^{1}H of terminal arenes), 2.9 (s, 3 H, Ar ^{1}H of bridging arene), 2.5 (s, 9 H, Me ^{1}H of bridging arene), 2.1 (s, 18 H, Me ^{1}H of terminal arenes); ^{13}C δ 82.5 (s, $C_{1,3,5}$ of terminal arenes), 74.9 (d, $^1J_{C-H}$ = 164 Hz, $C_{2,4,6}$ of terminal arenes), 64.7 (s, $C_{1,3,5}$ of bridging arene), 60.6 (d, $^1J_{C-H}$ = 171 Hz, $C_{2,4,6}$ of bridging arene), 21.2 (q, $^1J_{C-H}$ = 125 Hz, Me's of bridging arene), 20.3 (q, $^1J_{C-H}$ = 125 Hz, Me's of terminal arenes).

Both the ^{1}H and ^{13}C NMR spectra reveal the presence of mesitylene ligands in two different coordination environments and in the ratio of 2:1. The narrow line widths (<2 Hz) indicate that the complex is diamagnetic as would be expected for a 30-electron triple-decker sandwich structure.[16] The magnetic equivalency of related hydrogens and carbons in each arene ring is consistent with the high degree of symmetry in **2**. No evidence of fluxional behavior is apparent in the ^{1}H or ^{13}C NMR spectra down to −90 °C.[19] A noteworthy feature is the significant upfield shift of the

(1) Klabunde, K. J. *Chemistry of Free Atoms and Particles*; Academic Press: New York, 1980; pp 60-65.
(2) Blackborow, J. R.; Young, D. *Metal Vapour Synthesis in Organometallic Chemistry*; Springer-Verlag: New York, 1979; pp 119-136.
(3) Purchased from Torrovap Industries Inc.
(4) Cocondensation was conducted at 10^{-6} torr with cooling provided by a liquid nitrogen bath. Chromium was sublimed by resistive heating in dual, alumina-coated, tungsten wire crucibles at a rate of 0.75 g/h. Mesitylene was introduced through a heated shower head assembly at a rate of 1.25 mL/min. Reaction of 1.41 g of chromium with 130 mL of mesitylene under these conditions produced a dark frozen matrix which was allowed to thaw in vacuo. The resulting deep red solution was filtered through Celite and the filtrate evaporated to dryness at 10^{-3} torr and 40 °C. The remaining organometallic residue contained a 7.3/1.0 ratio of **1** and **2**, respectively, according to ^{1}H NMR analysis. The bis(mesitylene)chromium was sublimed at 65-70 °C and 10^{-3} torr leaving a nonvolatile residue which was enriched in **2**. This residue was recrystallized twice from petroleum ether at −30 °C yielding 100 mg of pure **2** in the form of dark thin plates.
(5) Attempts to grow single crystals suitable for X-ray crystallography have thus far been unsuccessful.

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(18) ^{1}H NMR spectra were recorded at 90 and 200 MHz; ^{13}C spectra were recorded at 50 MHz. NMR samples were prepared in toluene-d_8 or benzene-d_6. Chemical shifts are referenced to solvent resonances.
(19) The NMR data does not strictly rule out the existence of a less symmetrical butterfly structure similar to that found in the binuclear vanadium complex (C_5H_5)$_2$(C_6H_6)V_2H_2;[20] however, such a formulation would require that fluxional rotation of the face-bridging arene ring proceed with a very low activation barrier (<8 kcal/mol) and does not easily account for the matrix isolation evidence for the formation of higher nuclearity oligomers (vide infra).

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