that found in Cp$_3$U(*n*-Bu) of 2.43 (2) Å,[15a] and the U(2)–O distance of 2.11 (1) Å is similar to that found in [(Me$_5$C$_5$)$_2$U-(OMe)]$_2$PH of 2.05 (1) Å.[15b] The bond-length data support the view that the uranium atoms in the U(C$_5$H$_4$Me)$_3$ units are tetravalent and that the bridging phenyl isocyanate is best represented by the valence bond structure
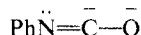
$$\overset{\cdot\cdot}{\text{Ph}\text{N}}\!\!=\!\!\overset{-}{\text{C}}\!\!-\!\!\overset{-}{\text{O}}$$

the result of a one-electron transfer from each (MeC$_5$H$_4$)$_3$U molecule. The PhNCO complex does not liberate CO on heating to 80 °C, nor do the nonequivalent MeC$_5$H$_4$ groups undergo site exchange.

Supplementary Material Available: Complete listing of bond lengths and angles for both crystal structures and positional and thermal parameters and all analytical data (11 pages). Ordering information is given in any current masthead page.

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## Stereocontrolled Syntheses of (*E*)- and (*Z*)-γ-Bisabolene 8,9-Epoxide

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γ-Bisabolene (**1**) is a naturally occurring sesquiterpene hydrocarbon[1] which on a speculative level is considered an important early intermediate in the biosynthesis of a variety of natural sesquiterpenoids.[2] However, only a few experimental works have been done in order to confirm either the *E* or *Z* isomeric forms of γ-bisabolene (**1a,b**) as real biogenetic intermediates,[3] or to exclude them as such,[4] which may be due to the fact that, despite the abundance of sesquiterpenes in nature and the variety of structural types, few compounds possessing the γ-bisabolene skeleton have been found in nature until recently. Chemical reports that permit a differentiation of both isomers, or which include an independent synthesis of each, have been published[5] and, as a result of these definitive studies,[5c] the proper identification of γ-bisabolene in natural systems can now be made.

The biosynthetic origin of the complex halogenated chamigrenes and related skeletal rearranged sesquiterpenes isolated from marine

(1) (a) Hochmannova, J.; Novotny, L.; Herout, V. *Collect. Czech. Commun.* **1962**, *27*, 1870. (b) Harrison, I. T. *An. Assoc. Bras. Quim.* **1962**, *21*, 23. (c) Heatherbell, D. A.; Wrolstad, R. E.; Libbey, L. M. *J. Food. Sci.* **1971**, *36*, 219. (d) Minyard, J. P.; Thumlinson, J. H.; Thomson, A. C.; Hedin, P. A. *J. Agric. Food Chem.* **1966**, *14*, 332.
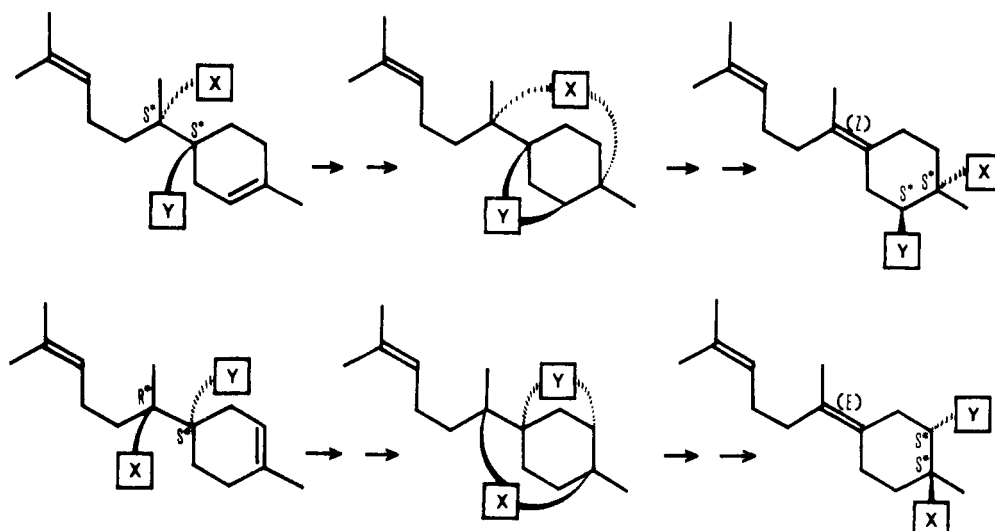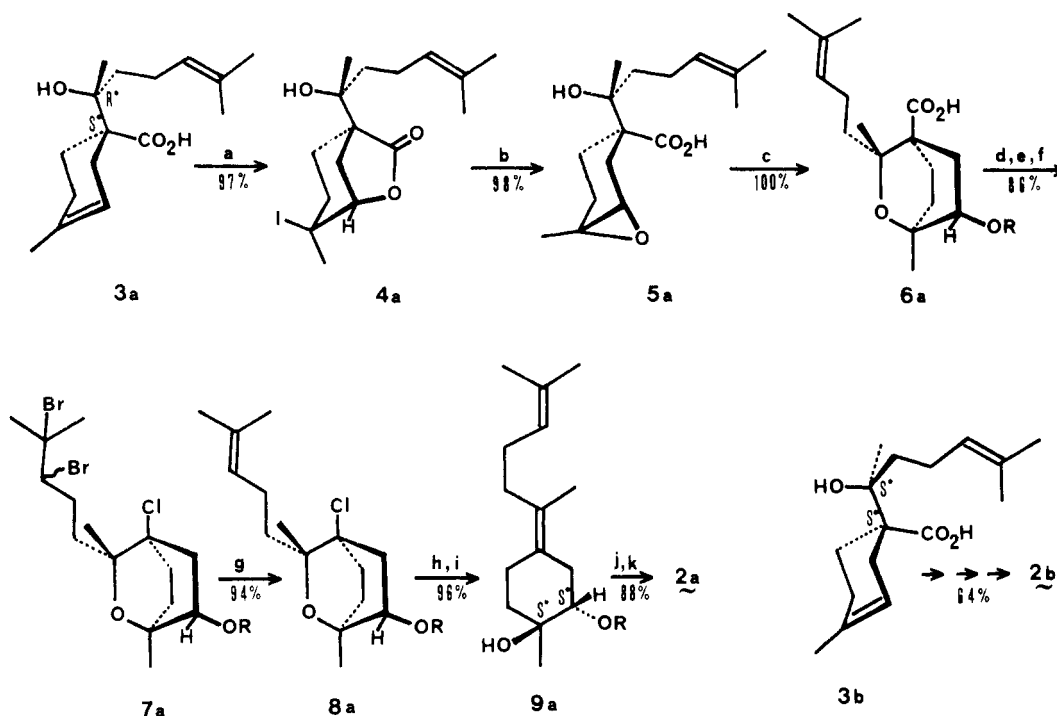(2) (a) Parker, W.; Roberts, J. S.; Ramage, R. *Q. Rev., Chem. Soc.* **1967**, *21*, 331. (b) Rücker, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 793. For an excellent recent review, see: (c) Cane, D. E. *Tetrahedron* **1980**, *36*, 1109.
(3) Anastasis, P.; Freer, I.; Gilmore, C.; Mackie, H.; Overton, K.; Swanson, S. *J. Chem. Soc., Chem. Commun.* **1982**, 260 and references cited therein.
(4) Adams, P. M.; Hanson, J. R. *J. Chem. Soc., Chem. Commun.* **1971**, 1415 and references cited therein.
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sources[6] has been the subject of recent discussions,[7] and pathways involving bromonium ion induced ring closure of γ-bisabolene (**1**) or γ-bisabolene 8,9-epoxide (**2**) have been proposed.[7d] As a part

1a   **1b**   **2a**   **2b**
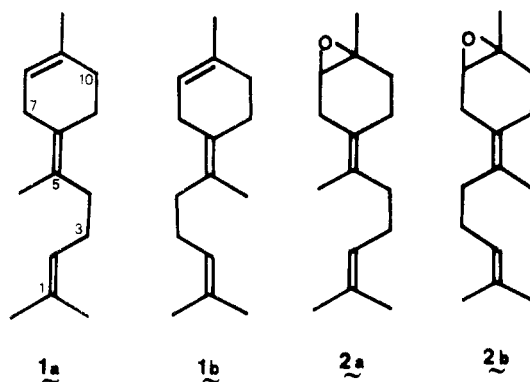
of our program on the synthesis of intermediates in terpene biogenesis and constituents of marine organisms, we have developed and record herein the first differentiated synthesis of the naturally found (*E*)-γ-bisabolene 8,9-epoxide (**2a**)[8] and its geometrical (*Z*)-isomer (**2b**), a discussion of which is the subject of this communication.

Neighboring group participation[9] is an established tool for reactivity control. It has been used for stereoselective introduction of functional groups,[10] selective protection,[11] double-bond transposition,[12] and to induce molecular conformational changes.[13] Racemic 8,9-trans-disubstituted (*E*)- and (*Z*)-γ-bisabolenes are synthesized here with regio- and stereocontrol by using simple forms of bridged intermediates (Scheme I). The control elements "X" and "Y" are inherent to the molecular organization of the starting material and are converted to *vicinal* groupings having defined stereochemistry in the final products. The stereochemistry of the tetrasubstituted olefinic bonds is controlled by bridging delivery from C$_5$ and C$_6$ positions.

The synthesis of (±)-**2a** (Scheme II) was initiated from the (±)-β-hydroxy acid **3a**, available[5c] on a large scale from 4-methyl-3-cyclohexenecarboxylic acid and 6-methyl-5-hepten-2-one in 85% yield, followed by fractional recrystallization of the diastereoisomeric **3a,b** mixture. Reaction of the diisopropylamine salt of **3a** with iodine in dichloromethane produced the iodo lactone **4a**[14] in 97% yield. Treatment of **4a** in THF with 1.5 equiv of aqueous potassium hydroxide at 0 °C for 2 h and isolation of the acidic product provided the unstable epoxy acid **5a** in 98% yield, which without further purification was treated with a catalytic amount of *p*-toluenesulfonic acid in methylene chloride to produce

(6) Faulkner, D. J. *Tetrahedron* **1977**, *33*, 1421. Martin, J. D.; Darias, J. In "Marine Natural Products"; Scheuer, P. J., Ed.; Academic Press: New York, 1978; Vol. 1, p 125. Fenical, W. In "Topics in the Biochemistry of Natural Products"; Waller, G. R., Ed.; Plenum Press: New York, 1979; Vol. 13, p 219. Erickson, K. L. In "Marine Natural Products"; Scheuer, P. J., Ed.; Academic Press: New York, 1983; Vol. 5, p 131. Faulkner, D. J. *Nat. Prod. Rep.* **1984**, *1*, 251.
(7) (a) Fenical, W. *J. Phycol.* **1975**, *11*, 245. (b) González, A. G.; Aguiar, J. M.; Martin, J. D.; Norte, M. *Tetrahedron Lett.* **1975**, 2499. (c) González, A. G.; Darias, J.; Diaz, A.; Fourneron, J. D.; Martin, J. D.; Pérez, C. *Tetrahedron Lett.* **1976**, 3051. (d) Suzuki, M.; Kowata, N.; Kurosawa, E. *Tetrahedron* **1980**, *36*, 1551.
(8) Suzuki, T.; Kikuchi, H.; Kurosawa, E. *Chem. Lett.* **1980**, 1267.
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(14) Satisfactory IR, ¹H NMR, and mass spectral data were obtained for each synthetic intermediate by using purified and chromatographically homogeneous samples. All chemical reactions were conducted under an inert atmosphere.

Scheme I

Scheme II[a]

[a] (a) I_2, 1.1 equiv in CH_2Cl_2, 1.0 M; add diisopropylamine salt of 3a, 1.0 equiv, 0 °C, 30 min; warm to room temperature, 30 min; 10% aqueous $Na_2S_2O_3$; workup with $NaHCO_3$ and hexane. (b) Preceding material, 1.0 equiv, 1.1 M in THF; KOH, 1.5 equiv in 2% aqueous THF, 1.1 M; 0 °C, 30 min, warm to 20 °C, 1 h; standard workup. (c) Preceding material, 1.0 equiv in CH_2Cl_2, 1.0 M; catalytic p-TSA; 0 °C, 10 min; standard workup. (d) 6a (R = H), Ac_2O, pyr, 25 °C, 6 h; standard workup; crystallized (hexane/CH_2Cl_2). (e) 6a (R = Ac), 1.0 equiv, in CCl_4, 0.5 M; 0 °C; Br_2, 1.1 equiv, in CCl_4, 0.25 M; stir until complete (TLC), 2 h; standard workup. (f) Preceding material, 2.4 equiv, and N-chloro-succinimide, 1.4 equiv, in DMF–HOAc (5:1), 1.5 M; add $Pb(OAc)_4$, 2.4 equiv, stabilized with ca. 15% HOAc; warm to 40–50 °C, 2 h; cooled solution extracted with pentane and washed with 2% $HClO_4$, 10% aqueous K_2CO_3, and water; filtration chromatography (silica gel, EtOAc/hexane, 2:3); crystallized (hexane/CH_2Cl_2). (g) 7a (R = H), 1.0 equiv, 0.5 M in ether–HOAc (5:1); 20.0 equiv, Zn dust, 4 h, 25 °C; workup with $NaHCO_3$ and hexane. (h) 8a (R = H), Ac_2O, pyr, 25 °C, 10 h; standard workup. (i) 8a (R = Ac), 1.0 equiv, 0.5 M in THF; 10.0 equiv, sodium metal, 0.01 M EtNH₂; 10 h, 0 °C; quenched with MeOH; standard workup; crystallization from Et_2O. (j) 9a (R = H), p-TsCl, pyr, 25 °C, 10 h, standard workup. (k) 9a (R = Ts), 1.0 equiv, 1.1 M in MeOH; KOH, 1.5 equiv in 10% aqueous MeOH, 1.1 M; 25 °C, 10 min, warm to 40 °C, 1 h, standard workup; filtration chromatography (silica gel, EtOAc/hexane, 1:4).

6a (R = H) in 100% yield. The sequence 3a–6a (R = H) can be carried out easily in the laboratory on a 1-mol scale, and the intermediates 4a and 5a need not be purified. Bromination (Br_2, CCl_4) of the crystalline acetate 6a (R = Ac) gave the dibromo derivative, which was decarboxylated,[15] by reaction with lead tetraacetate and N-chlorosuccinimide in DMF–HOAc (5:1), to give 7a (R = H) in 86% yield (10% of 6a (R = H) was recovered).

The dibromide 7a (R = H) was then subjected to reductive elimination of bromine by zinc dust (ether HOAc) to form the chloro ether 8a (R = H) which was purified by acetylation to give 8a (R = Ac). The reductive fission of the β-chloro ether bonds with powdered sodium metal in the presence of ethylamine and THF afforded the crystalline diene 9a (R = H) in 96% yield:[16]

(15) Becker, K. B.; Geisel, M.; Grob, C. A.; Kuhnen, F. *Synthesis* 1973, 493.

(16) For trans elimination of β-halo ethers similar to that described in this paper, see: Schlessinger, R. H.; Nugent, R. A. *J. Am. Chem. Soc.* 1982, *104*, 1116.

Other reagents such as zinc–silver couple[17] or magnesium (ether, THF) were ineffective. The overall yield of **9a** from **6a** was 79%.

Completion of the synthesis proceeded by tosylation (*p*-TsCl, C₅H₅N) of the diol **9a** (R = H) to yield the oily monotosyl derivative **9a** (R = Ts), which was converted to **2a** in 96% yield by treatment with aqueous potassium hydroxide in methanol. This racemic synthetic material gave NMR, MS, and IR spectra identical with those of a natural sample isolated from the red alga *Laurencia nipponica*.[8]

The synthesis of the *Z* isomer (±)-**2b** was accomplished starting from the diastereoisomeric β-hydroxy acid (±)-**3b**, following an identical sequence of reactions (64% overall yield).

Acknowledgment. We are indebted to the CAICYT for support of this work and express our gratitude to Professor E. Kurosawa (Hokkaido University) for providing spectral data of natural (*E*)-γ-bisabolene 8,9-epoxide.

Supplementary Material Available: Analytical data for **2a–4a**, **6a–9a**, **2b–4b**, and **6b–9b** (5 pages). Ordering information is given on any current mastehad page.

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Gas-Phase Platinum Cluster Reactions with Benzene and Several Hexanes: Evidence of Extensive Dehydrogenation and Size-Dependent Chemisorption

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Surface science, organometallic chemistry, and reaction kinetic studies on model systems have significantly improved our understanding of heterogeneous catalysis. We have initiated studies on the hopefully simpler system of unsupported platinum metal clusters to further our understanding of this chemistry. This work concentrates on two important steps, chemisorption of hydrocarbons under reaction conditions and their dehydrogenation.

We describe the first observation of reaction products of benzene, cyclohexane, 2,3-dimethylbutane, and *n*-hexane with gas-phase platinum clusters. Our major conclusions are that gas-phase platinum clusters dehydrogenate saturated hydrocarbons to a C/H ratio near 1 and exhibit a cluster-size-dependent extent of chemisorption.

These experiments were carried out on a pulsed molecular beam apparatus described elsewhere.[1] Metal clusters are produced by condensation of laser-vaporized (12-mJ doubled NdYAG) metal in a high-pressure helium flow. Reactions are carried out by pulsing reactant mixtures into the reactor to overlap the cluster pulse. The reaction conditions are estimated to be 0.1–1 atm of helium (0.2–0.4% reactant), 300–600 K[2], and a residence time of ~100 μs. Cluster reaction products are detected by photoionization (ArF 0.1–0.4 mJ/pulse) time-of-flight mass spectrometry. Low laser intensities were found necessary to minimize

(1) Rohlfing, E. A.; Cox, D. M.; Kaldor, A. *Chem. Phys. Lett.* **1983**, *99*, 161–166.

(2) The upper limit of 600 K was estimated from the fastest components' time-of-flight velocity distribution. This is in agreement with more accurate velocity measurements on iron clusters under similar conditions. Whetten, R. .; Cox, D. M.; Trevor, D. J.; Kaldor, A., submitted for publication in *J. Phys. Chem.*

(3) Dehydrogenation is defined as the observed mass loss with respect to Ptₙ(reactant)ₘ. In support of this, deuterium chemisorption was not found to occur on these small platinum clusters, under our reaction conditions, and is not stable on the most tightly bound states of the platinum metal surface above 380 K as reported by: Christmann, K.; Ertl, G.; Pignet, T. *Surf. Sci.* **1976**, *54*, 365–392.
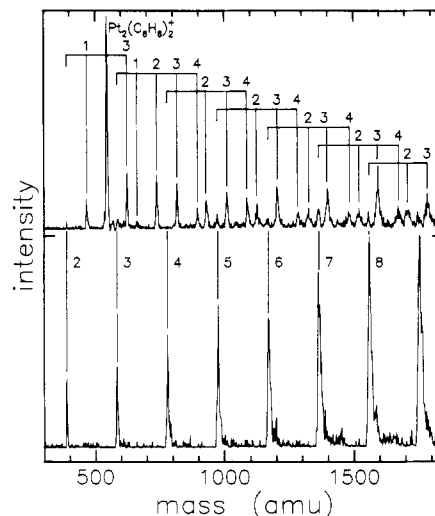
Figure 1. Time-of-flight mass spectra of platinum clusters after reactions with benzene. The lower trace is without reactant. The upper trace is with the pulsed addition of 0.21% benzene in helium. The notation indicates the number of adducts on each metal cluster. The metal clusters are all two-photon ionized, while the observed products are single-photon ionized; hence the enhancement of the product over metal signals.
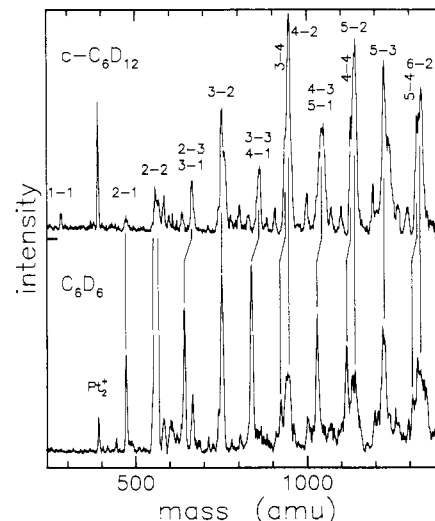
Figure 2. Time-of-flight mass spectra of platinum cluster reactions with benzene-d_6 (0.23% in helium) and with cyclohexane-d_{12} (0.25% in helium). The bis(benzene)diplatinum signal is off scale. The nomenclature used, *n*–*m*, stands for Ptₙ(adduct)ₘ. Lines are drawn between the spectra to point out the similarities in mass of many of the products produced.

multiphoton dissociative ionization.

Figure 1 shows our results of reacting benzene with platinum clusters. The lower spectrum represents the clean metal without overlap of the cluster and reactant pulses. The following are our observations: (1) The platinum atom monoadduct ion and diadduct parent ion signals are very weak. (2) The largest peak is the bis(benzene)diplatinum parent ion. (3) The mono- and triadducts on Pt₂ are observed. The monoadduct appears with a small degree of dehydrogenation. The tetradduct parent ion is present but very weak. (4) For larger clusters, the di- and triadducts dominate, while the monoadduct decreases in intensity. Above Pt₃ the benzene adducts begin to dehydrogenate, more so with the number of metal atoms than with the number of adducts.

Figure 2 shows the spectra for cyclohexane-d_{12} addition, and Figure 3 gives the results with *n*-hexane and 2,3-dimethylbutane. The following are our observations: (1) The mono- and diadducts are dehydrogenated to nearly an aromatic C/H ratio. (2) For cyclohexane the triadducts on Pt₂–Pt₄ are not as dehydrogenated. The deuterium loss on the Pt₂ and Pt₃ triadduct of cyclohexane-d_{12} is consistent with dehydrogenated diadducts plus cyclohexane-d_{12}.