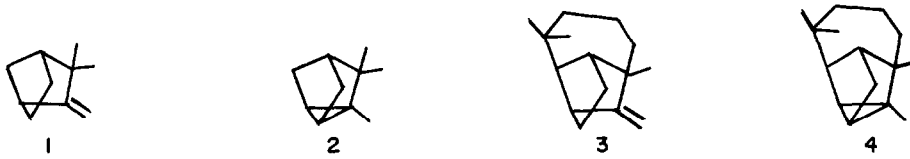


UNIQUE MERCURATION-HALOGENATION OF ISOPRENOID ECTOCYCLIC  
OLEFINS: NOVEL  $\omega$ -DIHALIDES FROM LONGIFOLENE AND CAMPHENE  
VIA  $\omega$ -DIMERCURICHLORIDES<sup>1</sup>

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In the field of isoprenoids, the monoterpene pair camphene 1 /  
tricyclene 2 and the closely related sesquiterpene pair longifolene 3 /  
longicyclene 4 display a typical brace of structural features:

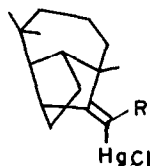


ectocyclic methylene/methylcyclopropane. The action of the soft acids Pb(IV)<sup>2a</sup>  
and Hg(II)<sup>2b</sup> on the cyclopropanic pair 2 / 4 has been studied by us recently  
and has generated interesting chemistry. A solvent-dictated novel product  
formation in the Pb(IV) oxidation<sup>3</sup> of the ectocyclic olefin pair 1 / 3 has  
also been observed. In this communication we describe the formation of exotic  
 $\omega$ -dimercurichlorides from the Hg(OAc)<sub>2</sub>/NaCl reaction on longifolene and  
camphene and their utility in the generation of the corresponding novel  
 $\omega$ -dihalides.

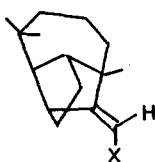
The structural and stereochemical outcome of the addition of Hg(OAc)<sub>2</sub>  
to olefins is consistent with the formation of an intermediate acetoxymercu-  
rium cation whose fate is dependent on the steric disposition of the double  
bond. In the case of a normal olefin, nucleophilic attack by acetate ion  
leading to 1-acetoxy-2-mercuriacetate derivative is the common pathway but in  
the case of hindered olefins, the acetoxymercurium ion loses a proton more  
rapidly than is attacked by a nucleophile, thus generating a vinyl mercuri-  
acetate<sup>4</sup>. In an attempt to rationalize the failure to achieve any hydration  
of longifolene 3 by the oxymercuration-demercuration sequence via the con-  
ventional in situ Hg(OAc)<sub>2</sub>/aq. THF-NaBH<sub>4</sub> reaction<sup>5</sup>, we invoked the formation  
of a vinylic mercurial of the type 5.

Treatment with aqueous NaCl of the gummy product from reaction of  
longifolene with Hg(OAc)<sub>2</sub> in AcOH (room temp./7 days) gave two pure

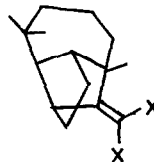
crystalline compounds isolated by a combination of crystallization ( $\text{CH}_2\text{Cl}_2$ ) followed by chromatography (silica gel): the more soluble minor compound (m.p.  $136^\circ$ ) was easily characterized as the expected  $\omega$ -mercurichloride 5 (14%); more interesting and quite unusual, however, was the less soluble, major compound (m.p.  $181^\circ$ ; 30%) - the  $\omega\omega$ -dimercurichloride 6.



5: R=H  
6: R=HgCl



7: X=Br  
9: X=I



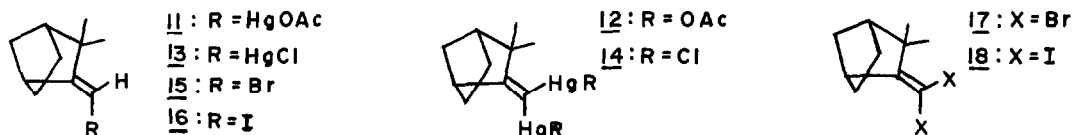
8: X=Br  
10: X=I

The PMR spectrum ( $\text{CCl}_4$ ) of compound 5 was characterized by a 1H vinylic singlet at 5.40 ppm and three tertiary methyl singlets at 0.97, 0.97 and 1.02 ppm. Unlike in the case of other  $\omega$ -substituted derivatives of longifolene, the allylic methine multiplet appeared at 2.60 ppm without suffering any downfield shift when compared to the parent longifolene case. The E-configuration for the double bond as shown in 5 has been derived from chemical evidence: generation of the known (E)- $\omega$ -bromolongifolene 7 (m.p.  $40^\circ$ ; 90%), on bromination of 5 in pyridine - a reaction known to proceed with retention of configuration<sup>6</sup>.

Spectral data of the major compound (m.p.  $181^\circ$ ) indicated a tetra-substituted double bond [PMR( $\text{CDCl}_3$ ): transparent olefinic region and allylic methine multiplet at 2.60 ppm; three tertiary methyl singlets at 0.97, 0.97, 1.20 ppm. IR (Nujol):  $1605\text{ cm}^{-1}$ ]. A unique  $\omega\omega$ -dimercurichloride structure 6, though unprecedented in the olefin-Hg(OAc)<sub>2</sub> reaction, was visualized as a mechanistically feasible working structure for the compound. Here again, bromination of the vinylic mercurial not only provided the crucial structural proof but also generated the novel  $\omega\omega$ -dibromolongifolene 8 (92%;  $\text{C}_{15}\text{H}_{22}\text{Br}_2$ ;  $M^+$  360, 362, 364). Validity of the assigned structure 8 for the dibromo-derivative (m.p.  $59^\circ$ ) was elegantly established when reductive elimination<sup>7</sup> of bromine ( $\text{Na}/\underline{t}\text{-BuOH}/\text{THF}$ ) furnished pure longifolene. Absence of any resonance above 3.13 ppm (no secondary bromide function) was an important supporting feature in the PMR spectrum of 8 (tertiary methyl singlets at 0.97, 0.97, 1.25 ppm).

The vinylic mercurials 5 and 6 have also been exploited to prepare novel iodo derivatives (corresponding to the bromo compounds 7 and 8) by simple treatment with ICl in pyridine at ambient temp.: 5  $\rightarrow$  9 (m.p.  $55^\circ$ ; 96%) and 6  $\rightarrow$  10 (m.p.  $129^\circ$ ; 74%). The PMR spectrum of  $\omega\omega$ -diiodo longifolene 10 ( $\text{C}_{15}\text{H}_{22}\text{I}_2$ ;  $M^+$  456) was similar to its dibromo analogue 8: allylic methine multiplet at 3.13 ppm and three tertiary methyl singlets at 1.00, 1.00 and 1.27 ppm. Reductive elimination, as in the case of 8, generated longifolene.

In a comparative study, the camphene-Hg(OAc)<sub>2</sub> reaction product was amenable to direct crystallization (without NaCl treatment) and two pure crystalline compounds were isolated by a combination of crystallisation (CH<sub>2</sub>Cl<sub>2</sub>-hexane) and chromatography. The minor compound (22%) and the major compound (29%) were readily characterized as the ω-mercuriacetate 11 and the ω-dimercuriacetate 12. Furthermore, the ω-mercurichloride 13 and the



ω-dimercurichloride 14 were easily generated from 11 and 12 respectively by exposure to aqueous NaCl. As in the case of longifolene, Hg-free ω-halogenated derivatives were readily prepared from camphene vinylic mercurials by reaction with Br<sub>2</sub> or ICl in pyridine. Some physical data of the camphene vinylic mercurials/ω-halo derivatives are given in Table I.

TABLE I

Compd.	m.p./ b.p. (bath)	PMR values <sup>+</sup> (ppm)			
		vinylic H	allylic H	OAc	tertiary Me
<u>11</u>	77°	5.27(s)	2.70(m)	1.93(s)	1.10(s), 1.10(s)
<u>13</u>	103°	5.35(s)	2.67(m)	-	1.08(s), 1.08(s)
<u>15</u>	90°/0.7 mm	5.57(s)	3.13(m)	-	1.10(s), 1.10(s)
<u>16</u>	105°/1 mm	5.52(s)	3.03(m)	-	1.08(s), 1.08(s)
<u>12</u>	196°	-	2.70(m)	2.08(s), 2.08(s)	1.30(s), 1.25(s)
<u>14</u>	270°d	-	2.63(m)	-	1.27(s), 1.22(s)
<u>17</u> <sup>8</sup>	130°/0.5 mm	-	3.13(m)	-	1.30(s), 1.25(s)
<u>18</u> <sup>8</sup>	150°/0.3 mm	-	3.13(m)	-	1.35(s), 1.28(s)

<sup>+</sup>in CCl<sub>4</sub> except for 12 (CDCl<sub>3</sub>) and 14 (pyridine)

Two other points of interest may be mentioned: (1) further reaction of Hg(OAc)<sub>2</sub> in AcOH (room temp./3 days; NaCl work-up) converted the vinylic monomercurials into the dimercurials - 5 → 6 (67%); 13 → 14 (83%) and (ii) the vinylic mercurials from longifolene (5 and 6) and from camphene (13 and 14) underwent smooth reductive elimination on reaction with LiAlH<sub>4</sub> to furnish the parent olefins.

## REFERENCES AND NOTES

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In the case of camphene 1, Hg(OAc)<sub>2</sub>/aq. THF reaction (room temp./5 hr) followed by in situ NaBH<sub>4</sub> reduction, readily furnished the expected tertiary alcohol (26%); under the same reaction conditions longifolene failed to undergo any hydration and the isolated product consisted of only longifolene.
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- 8 Reductive elimination (Na/THF/t-BuOH) generated camphene.

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