

UNIQUE MERCURATION-HALOGENATION OF ISOPRENOID ECTOCYCLIC
OLEFINS: NOVEL $\omega\omega$ -DIHALIDES FROM LONGIFOLENE AND CAMPHENE
VIA $\omega\omega$ -DIMERCURICHLORIDES¹

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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:

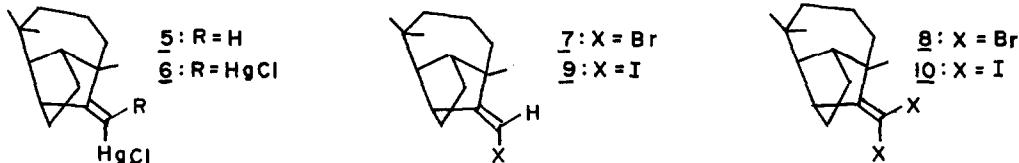


ectocyclic methylene/methylcyclopropane. The action of the soft acids Pb(IV)^{2a} and Hg(II)^{2b} on the cyclopropanic pair 2 / 4 has been studied by us recently and has generated interesting chemistry. A solvent-dictated novel product formation in the Pb(IV) oxidation³ of the ectocyclic olefin pair 1 / 3 has also been observed. In this communication we describe the formation of exotic $\omega\omega$ -dimercurichlorides from the $\text{Hg(OAc)}_2/\text{NaCl}$ reaction on longifolene and camphene and their utility in the generation of the corresponding novel $\omega\omega$ -dihalides.

The structural and stereochemical outcome of the addition of Hg(OAc)_2 to olefins is consistent with the formation of an intermediate acetoxymercurium 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-acetate⁴. In an attempt to rationalize the failure to achieve any hydration of longifolene 3 by the oxymercuration-demercuration sequence via the conventional in situ $\text{Hg(OAc)}_2/\text{aq. THF-NaBH}_4$ reaction⁵, 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)_2 in AcOH (room temp./7 days) gave two pure

crystalline compounds isolated by a combination of crystallization (CH_2Cl_2) followed by chromatography (silica gel): the more soluble minor compound (m.p. 136°) was easily characterized as the expected ω -mercurichloride 5 (14%); more interesting and quite unusual, however, was the less soluble, major compound (m.p. 181° ; 30%) - the $\omega\omega$ -dimercurichloride 6.

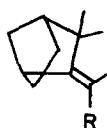


The PMR spectrum (CCl_4) of compound 5 was characterized by a 1H vinylic singlet at 5.40 ppm and three tertiary methyl singlets at 0.97, 0.97 and 1.02 ppm. Unlike in the case of other ω -substituted derivatives of longifolene, the allylic methine multiplet appeared at 2.60 ppm without suffering any downfield 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)- ω -bromolongifolene 7 (m.p. 40° ; 90%), on bromination of 5 in pyridine - a reaction known to proceed with retention of configuration⁶.

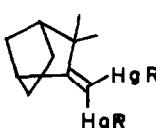
Spectral data of the major compound (m.p. 181°) indicated a tetra-substituted double bond [PMR(CDCl_3): transparent olefinic region and allylic methine multiplet at 2.60 ppm; three tertiary methyl singlets at 0.97, 0.97, 1.20 ppm. IR (Nujol): 1605 cm^{-1}]. A unique $\omega\omega$ -dimercurichloride structure 6, though unprecedented in the olefin-Hg(OAc)₂ 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°) was elegantly established when reductive elimination⁷ of bromine ($\text{Na}/t\text{-BuOH}/\text{THF}$) 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° ; 96%) and 6 \rightarrow 10 (m.p. 129° ; 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.

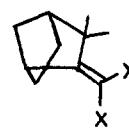
In a comparative study, the camphene- Hg(OAc)_2 reaction product was amenable to direct crystallization (without NaCl treatment) and two pure crystalline compounds were isolated by a combination of crystallisation (CH_2Cl_2 -hexane) and chromatography. The minor compound (22%) and the major compound (29%) were readily characterized as the ω -mercuriacetate 11 and the $\omega\omega$ -dimercuriacetate 12. Furthermore, the ω -mercurichloride 13 and the



11: $\text{R} = \text{HgOAc}$
13: $\text{R} = \text{HgCl}$
15: $\text{R} = \text{Br}$
16: $\text{R} = \text{I}$



12: $\text{R} = \text{OAc}$
14: $\text{R} = \text{Cl}$



13: $\text{R} = \text{Cl}$
17: $\text{X} = \text{Br}$
18: $\text{X} = \text{I}$

$\omega\omega$ -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_2 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 ⁺ (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), 1.30(s), 1.25(s) 2.08(s)	
<u>14</u>	270°d		2.63(m)	-	1.27(s), 1.22(s)
<u>17</u> ⁸	130°/0.5 mm	-	3.13(m)	-	1.30(s), 1.25(s)
<u>18</u> ⁸	150°/0.3 mm	-	3.13(m)	-	1.35(s), 1.28(s)

⁺in CCl_4 except for 12 (CDCl_3) and 14 (pyridine)

Two other points of interest may be mentioned: (i) further reaction of Hg(OAc)_2 in AcOH (room temp./3 days; NaCl work-up) converted the vinylic monomercurials into the dimercurials - 5 \rightarrow 6 (67%); 13 \rightarrow 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_4 to furnish the parent olefins.

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In the case of camphene 1, $Hg(OAc)_2$ /aq. THF reaction (room temp./5 hr)
followed by in situ $NaBH_4$ 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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