

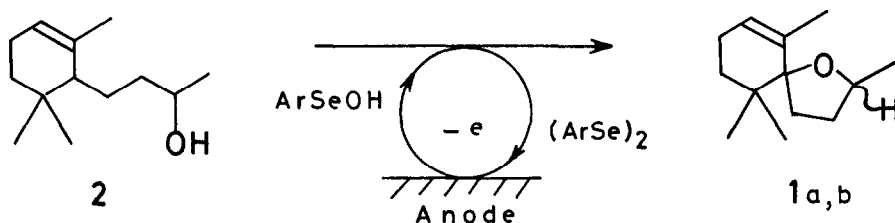
**A NOVEL SELENIUM-MEDIATED SPIROANNELATION : ONE-STEP PREPARATION
OF dl-THEASPIRANE FROM α -DIHYDROIONOL**

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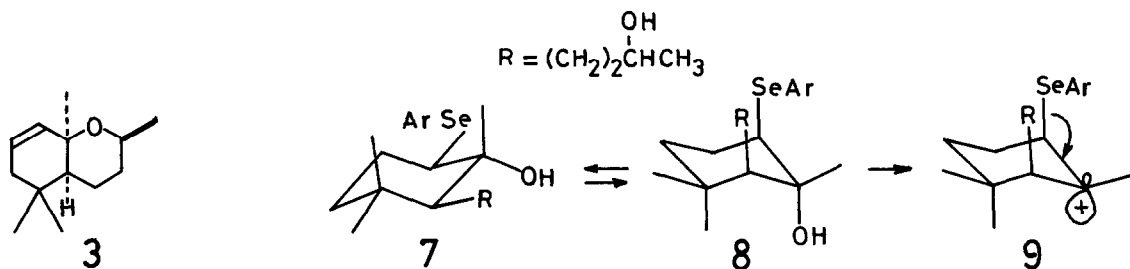
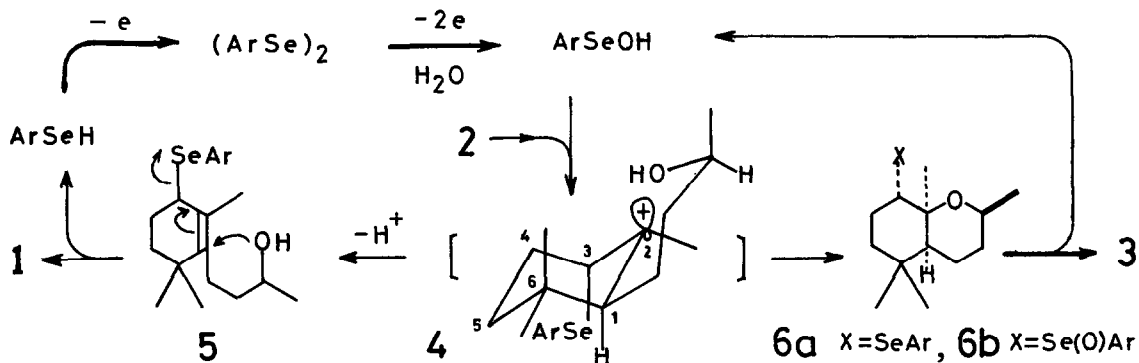
summary: dl-Theaspirane (1) was prepared by the selenium-mediated electrochemical oxidation of α -dihydroionol (3), via a novel selenium-mediated spiroannellation.

Electrophilic addition of organoseleno group to C=C double bond and the subsequent oxidative deselenation via selenoxide has been well documented.¹⁾ However, the electrophilic ene-type addition of selenium followed by displacement of the seleno group by nucleophile at γ -position is unknown. Here, we describe an electrochemical one-step preparation of dl-theaspirane (1)²⁾, a black tea aroma, from dl-dihydroionol (2) to demonstrate a novel selenium-mediated spiroannellation which involves the addition of arylseleno group to C=C double bond and the subsequent elimination of the seleno group as a selenide anion.



A mixture of 2³⁾ (118 mg, 0.6 mmol), bis(p-chlorophenyl) diselenide (17 mg, 0.06 mmol), Et₄NC10₄ (100 mg), and MgSO₄ (300 mg) dissolved in MeCN (7 ml)-H₂O (0.2 ml) was electrolyzed in an undivided cell under a constant current (Pt, 20 mA, 8 F/mol) at 65 - 70 °C, affording 1 (70%, 1a : 1b = 50 : 50 by vpc, SE-30, 6 m-4 ϕ , 130 °C) along with dl-dihydroedulan (3)⁴⁾ (18%). Likewise, electrolysis of 2 in CH₂Cl₂ in the presence of 50 mol % of the diselenide provided 1 (78%) and 6a (12%). Hydrogen peroxide oxidation of 6a gave 3. In contrast, the action of a stoichiometric amount of phenylselenenyl chloride in the same conditions of the electrolysis provided only 24% of 1 and none of 3.⁵⁾ The oxidation of the diselenide is essential for the transformation (2 \rightarrow 1) since none of 1 is produced by electrolysis in the absence of the diselenide. Diaryl diselenide is electrochemically oxidized to generate an active selenating reagent⁷⁾ which attacks double bond of 2 from α -

face, providing carbenium ion 4. Deprotonation from C-1 of 4 results in 5 which immediately releases arylselenide anion⁸⁾ to give 1. Arylselenol produced in this step (5→1) would be oxidized successively at the anode, regenerating arylselenenic acid via the corresponding diselenide for the recycle use. The facile deprotonation from C-1 of 4 is due to the stereochemically favorable anti-staggered conformation of H-1 to the lobe of the incipiently formed carbenium ion. In fact, carbenium ion 9 generated by formic acid and boron trifluoride-catalyzed dehydroxylation of the alcohol 7 underwent an exclusive deselenation leading to the formation of 2 rather than deprotonation from C-1. Meanwhile, the intramolecular trapping of the cation 4 by hydroxyl group occurs competitively to give 6a, which is oxidatively transformed into 3.



- 1) D. L. Clive, *Tetrahedron*, **1978**, 34, 1049; H. J. Reich, *Acc. Chem. Res.*, **1979**, 12, 22.
- 2) K. H. Schulte-Elte, F. Gautschi, W. Renold, A. Hauser, P. Fankhauser, J. Limacher, G. Ohloff, *Helv. Chim. Acta*, **1978**, 61, 1124. H. Etoh, K. Ina, M. Iguchi, *Agric. Biol. Chem.*, **1980**, 44, 2871 and references cited therein.
- 3) α -Dihydroionol 2 [purity; α (92%) and β (6%)] was supplied by Soda Perfume Co. Ltd.
- 4) G. D. Prestwich, F. G. Whitfield, G. Stanley, *Tetrahedron*, **1976**, 32, 2945.
- 5) Hydrogen chloride is formed under the reaction conditions where 1 and 3 are unstable.⁶⁾
- 6) H. Okawara, S. Kobayashi, M. Ohno, *Heterocycles*, **1979**, 13, 191.
- 7) S. Torii, K. Uneyama, M. Ono, T. Bannou, *J. Am. Chem. Soc.*, **1981**, 103, 4606.
- 8) H. Nishiyama, K. Itagaki, K. Sakuta, K. Itoh, *Tetrahedron Lett.*, **1981**, 22, 5285.
- K. B. Sharpless, R. F. Lauer, *J. Org. Chem.*, **1972**, 37, 3973.

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