

A NOVEL SYNTHESIS OF DL-MARMELOLACTONE AND DL-ROSE OXIDE BY
ELECTROCHEMICAL OXYSELENYLATION-DESELENYLATION SEQUENCE

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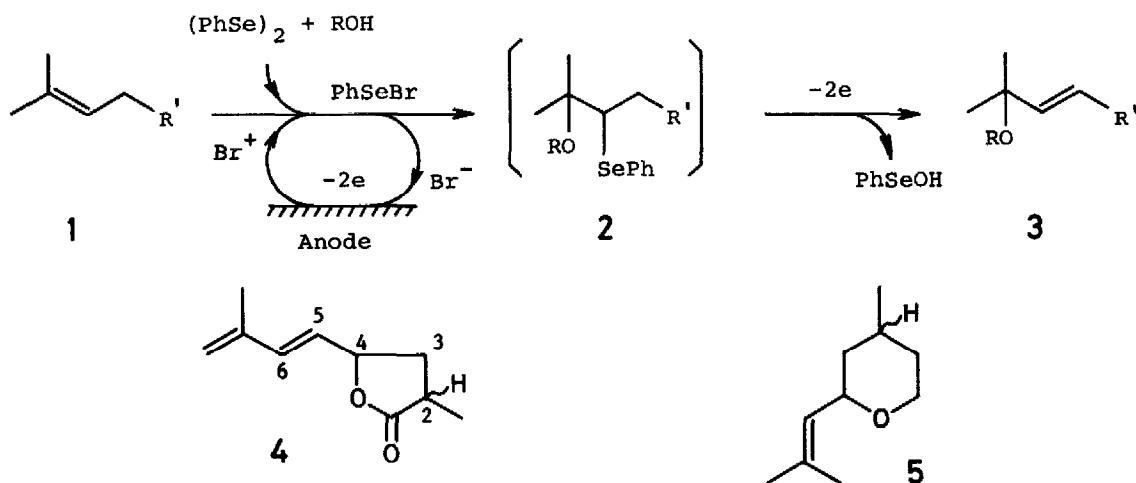
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Summary One-step transformation of olefins 1 into allylic alcohols and ethers 3 has been accomplished by electrooxidative oxyselenenylation-deselenenylation sequence. The electrochemical process furnished efficient syntheses of dl-marmelolactone 4 and dl-rose oxide 5.

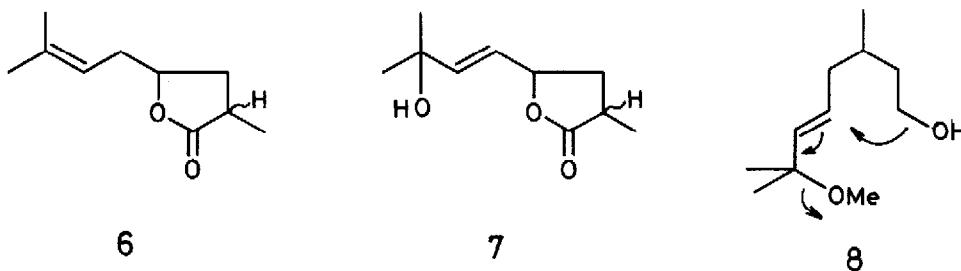
Our recent discovery of an electrochemical oxyselenenylation of olefins (1 → 2)¹⁾ prompted us to develop an one-step transformation of olefins 1 into allylic alcohols and ethers 3 by an electrooxidative oxyselenenylation-deselenenylation sequence. The highly selective electrochemical process enables us to prepare 3 in very simple and mild reaction conditions without use of activated selenenylating reagents (PhSeX, X = Cl, Br, OH, NR₂) and peroxides.²⁾

Here we describe a preliminary result of the transformation (1 → 3) and its application to syntheses of dl-marmelolactone 4, recently isolated from a volatile and characteristic sweet odorous constituent of Japanese quince or marmelo,³⁾ and dl-rose-oxide 5.

A typical electrolysis is as follows; A solution of 6 (1 mmol),³⁾ (PhSe)₂ (0.5 mmol), and Et₄NBr (0.1 mmol) in H₂O (2 ml)-MeCN (6 ml) was electrolyzed using Pt foils (2 x 1.5 cm²) in an undivided cell at room temperature (constant current 40 mA, 16.5 F/mol).⁴⁾ The usual working-up and chromatographic purification provided 7 (J₅₆ = 15.6 Hz) in 85% yield.



Similarly, electrolysis of citronellol 1 ($R' = \text{CH}_2\text{CH}(\text{Me})\text{CH}_2\text{CH}_2\text{OH}$) in MeOH ($\underline{1} = 1 \text{ mmol}$, $(\text{PhSe})_2 = 0.5 \text{ mmol}$, $\text{Et}_4\text{NBr} = 0.05 \text{ mmol}$, 30 mA , 8 F/mol) afforded 8 (89%, $J_{56} = 15.6 \text{ Hz}$). Particularly noteworthy are the facts that a trace amount of Et_4NBr is enough for completion of the reaction and that about 15% of $(\text{PhSe})_2$ was recovered. Presumably, diphenyl diselenide arises by cathodic reduction or disproportionation of phenylselenenic acid.⁵⁾ Actually, electrolysis of 2 ($R' = \text{CH}_2\text{CH}(\text{Me})\text{CH}_2\text{CH}_2\text{OH}$, $R = \text{Me}$)¹⁾ produced $(\text{PhSe})_2$ along with 8. The mechanism of the transformation ($\underline{1} \rightarrow \underline{3}$) is assumed as follows; The electrochemically generated Br^+ reacts with $(\text{PhSe})_2$ to form PhSeBr , which attacks 1 followed by solvolysis (ROH) to give 2.¹⁾ The subsequent electrooxidation of 2 gives the corresponding selenoxide in situ, which undergoes deselenenylation to provide 3.



Treatment of 7 with methanesulfonyl chloride in the presence of triethylamine in CH_2Cl_2 provided 4 (83%). While, thermal dehydration of 7 proceeded at 150°C in the presence of KHSO_4 to give 4 (68%). The synthetic 4 was a mixture of cis and trans-isomers on 2-Me and 4-alkenyl groups (cis/trans = 4/6 by HPLC) and the ^1H NMR and IR spectra of the separated isomers (HPLC) were consistent with those of the natural samples.³⁾

Transformation of 8 into dl-rose oxide 5 was accomplished by demethoxylation of 8 on treatment with BF_3 -etherate in CH_2Cl_2 at room temperature (94%, 84% from citronellol). The synthetic 5 was a mixture of cis and trans rose oxide (cis/trans = 4.4/1 by vpc) and its spectral data were superimposable with those of the authentic samples.

References and Notes

- 1) S. Torii, K. Uneyama, and M. Ono, *Tetrahedron Lett.*, in press.
- 2) Two-step conversion of olefins into allylic alcohols and their derivatives (oxyselenenylation of olefins with PhSeX followed by oxidative deselenenylation with peroxides) is described. T. Hori and K. B. Sharpless, *J. Org. Chem.*, **43**, 1689 (1978); D. L. J. Clive, *Tetrahedron*, **34**, 1049 (1978); H. J. Reich, *Acc. Chem. Rec.*, **12**, 22 (1979).
- 3) T. Tsuneya, M. Ishihara, Y. Shiota, and M. Shiga, *Agric. Biol. Chem.*, **44** (4) (1980) in press. The authors are grateful to Messrs T. Tsuneya, M. Ishihara, Y. Shiota, and M. Shiga for their kind gift of 6 (cis/trans = 4/6 by HPLC) and spectral data of the natural 4.
- 4) Oxyselenide 2 can be selectively prepared by electrolysis in the presence of a trace amount of sulfuric acid. (Ref. 1) Details on the mechanism and scope and limitation of the transformation ($\underline{1} \rightarrow \underline{3}$) will be described elsewhere.
- 5) H. J. Reich, S. Wollowitz, J. E. Trend, F. Chow, and D. F. Wendelbron, *J. Org. Chem.*, **43**, 1697 (1978); O. Berhagel and H. Seibert, *Chem. Ber.*, **66**, 708 (1933).

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