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ELECTROORGANIC CHEMISTRY IX

ANODIC CYCLIZATION OF OLEFINIC ALCOHOLS TO CYCLIC ETHERS

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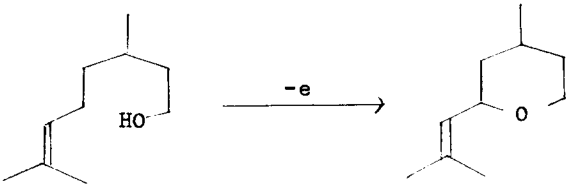
The electrode reaction of organic compound is a growing and interesting subject in the field of the organic synthesis. In the previous report of this series, the anodic allylic substitution of some aliphatic olefins in several nucleophilic solvents was studied.1)

In the present study, we wish to report a novel method of synthesis of cyclic ethers by anodic oxidation of olefinic alcohols.

The electrode reaction was performed at room temperature using carbon electrodes under the condition of constant current. The supporting electrolyte was tetraethylammonium p-toluenesulfonate (**1**).

The electrooxidation of citroneroll (**2**) (1.0 mole/l) in acetonitrile was carried out at a current density of 40 mA/cm^2 and a working anode potential of 1.8 V (vs.sce). After 2.0 Faraday/mole of electricity was passed, rose oxide (**3**) was obtained in a 26% yield.



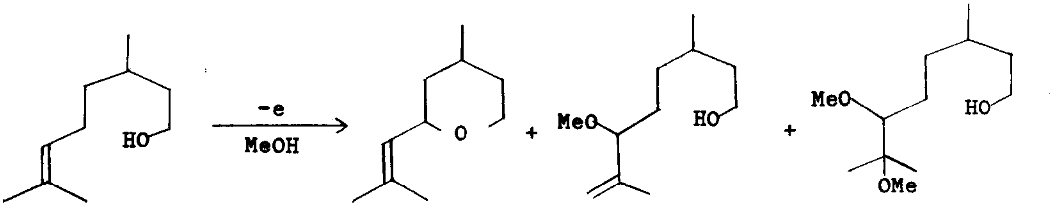
2 **3**

The current efficiency of the formation of **3** decreased with the increase in the current density, while it exhibited a maximum value at 1.0 mole/l of the concentration of 3.

The ratio of cis to trans isomers of the rose oxide obtained (71/29) was quite similar to that of natural rose oxide. An optically active ℓ-citroneroll ($[\alpha]_D^{25}$ -4.8°) afforded an optically active rose oxide ($[\alpha]_D^{25}$ -39.3°) where the optical rotation was close to the best value of the natural compound. (-41.5°).[2)]

Although, a number of synthetic methods of rose oxide from citroneroll have been reported,[2)-4)] the present electrochemical method would be of great advantage to the previous methods.

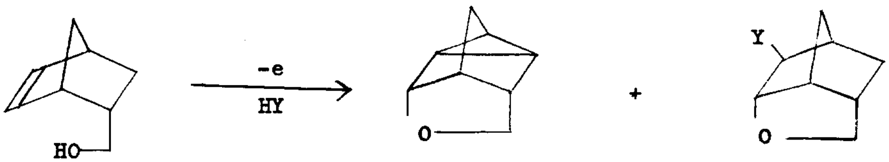
The anodic oxidation of citroneroll in methanol gave 7.0% of **3**, 31.5% of 2.6-dimethyl-3-methoxyoct-1-ene-8-ol (**4**) and 10.5% of 2.6-dimethyl-2,3-dimethoxyoctanol-8 (**5**)



2 **3** **4** **5**

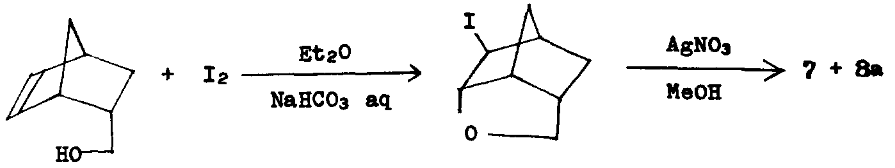
In acetic acid or propylene carbonate, the yield of **3** was 10.0% or 18.8%, respectively.

The anodic oxidation of endo-norbornenemethanol (**6**) in acetonitrile (40 mA/cm^2, 1.8V vs.sce, 2.0 Faraday/mole) formed 2-oxa-tetracyclo [4.2.1.0.^{4,8} 0^{5,9}] nonane (**7**) in a 13.8% yield. In methanol, 22.3% of **7** and 12.0% of exo-9-methoxy-2-oxa-tricyclo [4.2.1.0.^{4,8}] nonane (**8a**) were obtained. Furthermore, in acetic acid (1.0 Faraday/mole) the products were 6.0% of **7** and 2.8% of exo-9-acetoxy-2-oxatricyclo [4.2.1.0^{4,8}] nonane (**8b**).



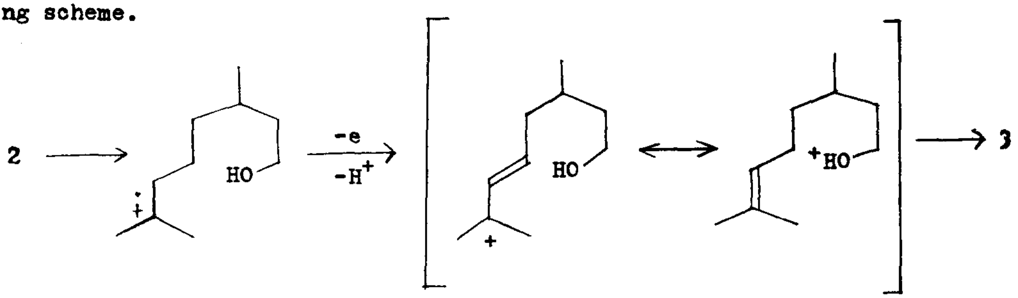
6 **7** **8a** (Y=OMe) **8b** (Y=OAc)

Compounds 7 and 8a were synthesized by the route shown in the following scheme, and the structures of 7 and 8a were thereby established.

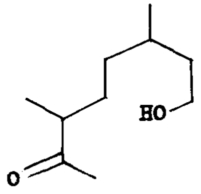


Compound 7 had bp 63°~64° (17 mm); nmr spectrum (in CCl_4), τ 8.83 (broad singlet, 3H), 8.33 (broad singlet, 2H), 8.09 (multiplet, 1H), 7.69 (mulitiplet, 1H), 6.29 (doublet, J 1Hz, 2H), 5.88 (doublet, J 2Hz, 1H)

This anodic cyclization would proceed according to the similar reaction mechanism to what was suggested for the anodic allylic substitution where the initiation step is the anodic oxidation of the olefinic bond to a cation radical. The mechanism of the formation of 3 from 2 is shown in the following scheme.



Furthermore, in the oxidation of citroneroll in methanol, the formation of 4 and 5 under an anhydrous condition or that of 3,6-dimethyl-8-hydroxy-octanone-2 (10) under the existence of moisture would imply the adequency of this mechanism. The proton elimination from the homoallylic position of 6 yields the product 7, since the ejection of a proton from the allylic position of 6 may be difficult.



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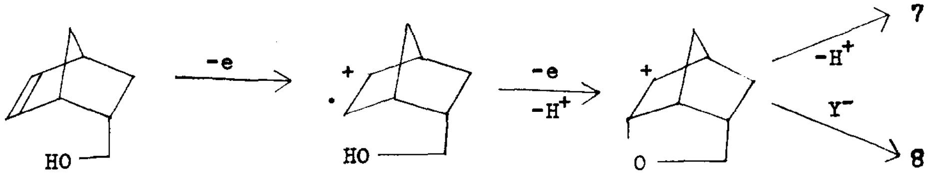

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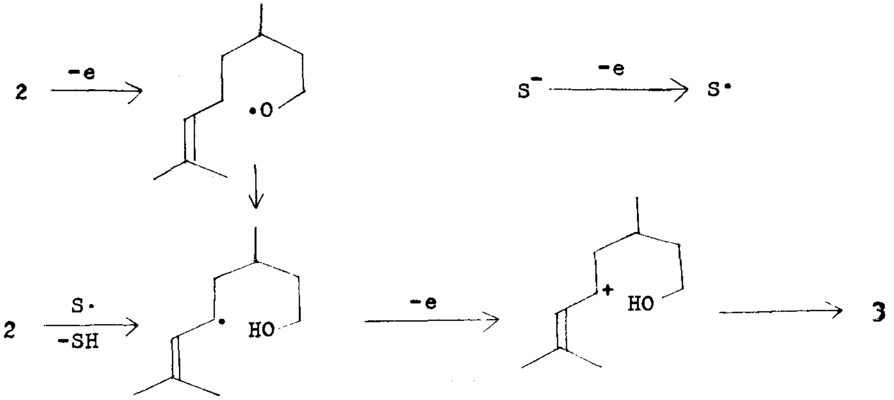
On the other hand, as shown in the following scheme, the reaction route initiated by the hydrogen abstraction with the anodically generated radicals might be another possibility. (S^-; Anionic part of supporting electrolyte)



The fact that a trace amount (< 0.2%) of 2-methyltetrahydrofuran was yielded in the anodic oxidation of n-amylalcohol in acetonitrile makes it reasonable to presume that at least a minor portion of the present anodic cyclization reaction proceeded according to the above radical initiation route.

References

(1) T.Shono and T.Kosaka, Tetrahedron Letters No59 6207 (1968)

(2) C.F.Seidel, Dorothee Felix, A.Eschenmoser, K.Biemann, E.Palluy and M.Stoll Helv. Chim. Acta., 44 598 (1961)

(3) G.Ohloff and B.Lienhard ibid, 48 182 (1965)

(4) G.Ohloff, K.H.Schulte-Elte and B.Willhalm ibid 47 602 (1964)