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A NOVEL SYNTHESIS OF ℓ-CARVONE FROM ℓ-α-PINENE

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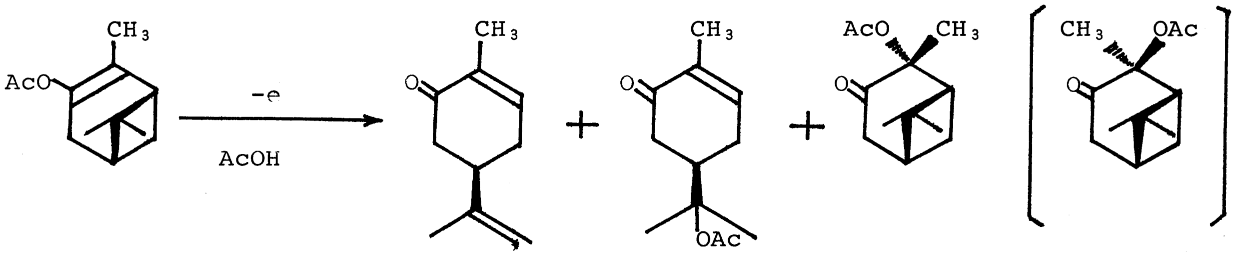
A novel synthetic method of ℓ-carvone involving the anodic oxidation of the enol acetate of isopinocamphone in the mixed solvent of methylene chloride-acetic acid as a key step was established. The overall yield of ℓ-carvone from ℓ-α-pinene was 34% and the overall optical yield was quantitative.

Hitherto known typical synthetic method¹⁾ of ℓ-carvone(**4**) involves the addition of nitrosyl chloride to d-limonene followed by dehydrochlorination and hydrolysis. In our recent study on the electrooxidation of carbon-carbon double bonds, it was demonstrated 2) that the anodic oxidation of α-pinene (**1**) in acetic acid gave carveol and p-menth-6-ene-2,8-diol derivatives indicating the specific opening of the four membered ring of α-pinene. Moreover, the exclusive formation of the α,β-unsaturated enones by the anodic oxidation of α-alkylated alicyclic enol acetates has been established in our previous study. 3) These two findings may suggest the availability of the anodic method in the conversion of the enol acetate(**3**) of ℓ-isopinocamphone to ℓ-carvone(**4**). The starting enol acetate (**3**) was readily prepared through hydroboration 4) of ℓ-α-pinene(**1**) followed by the oxidation 5) of the resulting alcohol with Jones' reagent and subsequent treatment of the resulting ℓ-isopinocamphone(**2**) 6,7) with isopropenyl acetate.

The anodic oxidation of the enol acetate(**3**) in acetic acid yielded three types of products, namely ℓ-carvone(**4**), 8-acetoxy-p-menth-6-en-2-one(**5**) 8) and unrearranged acetoxy ketone(**6**). 9) Their yield were largely dependent on the nature of the solvent and the supporting electrolyte. Typical results are summarized in Table I. All of these three products were characterized by the comparison of their spectroscopic and gas chromatographic behaviors with those of authentic samples. The stereoisomer(**7**) of the acetoxy ketone(**6**) was also prepared from thermolysis9) of the epoxidation product of the enol acetate(**3**), but none of **7** was found in the product of the anodic oxidation of **3**.



3 **4** **5** **6** **7**

Table I Anodic Oxidation of The Enol Acetate(**3**)[a,b]

Run	Solvent	Supporting Electrolyte	Product(%)[c]		
			4	**5**	**6**
1	AcOH	Et_4NOTs	31	23	0
2	AcOH	AcOK	9	8	36
3	MeOH	Et_4NOTs	15	43[d]	0
4	CH_2Cl_2-AcOH(4:1)	Et_4NOTs	36	15	0
5	CH_2Cl_2-AcOH(8:1)	Et_4NOTs	64	0	0
6	CH_2Cl_2-AcOH(50:1)	Et_4NOTs	19	0	0
7	CH_2Cl_2-CH_3CN(8:1)	Et_4NOTs	6	0	0

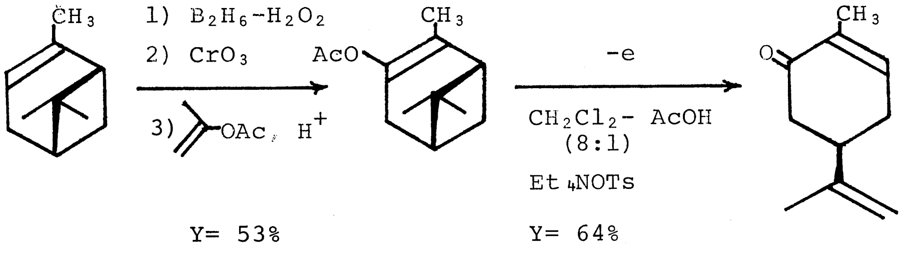
a: The electrolysis was continued until 4 F/mol of electricity was passed.

b: The electrolysis was carried out using carbon electrodes at room temperature.

c: The yield was determined by the gas chromatographic technique using benzyl cyanide as an internal standard.

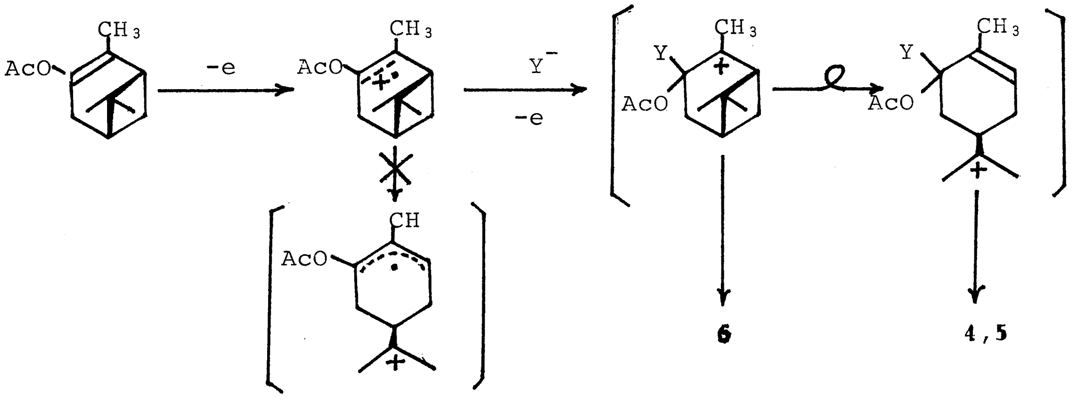
d: 8-Methoxy-p-menth-6-en-2-one.

As shown in Table I, the anodic oxidation of **3** in the mixed solvent(8:1) of methylene chloride-acetic acid containing tetraethylammonium p-toluenesulfonate as a supporting electrolyte gave almost pure **4** in a 64% yield. The overall yield of **4** starting from ℓ-**1** was 34% and the overall optical yield was quantitative.10)



ℓ-**1** **3** **4**

As was discussed in our previous study,2,3) the formation of the ring-opened products,(**4**)and(**5**),and the unrearranged acetoxy ketone(**6**)may be explained by the following mechanism.



8 Y= AcO or OTs

The quantitative optical yield would exclude the formation of an allylic type intermediate such as **8**. The specific opening of the four membered ring of α-pinene moiety is noteworthy.

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