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A NOVEL SYNTHESIS OF l-CITRONELLOL FROM l-MENTHONE

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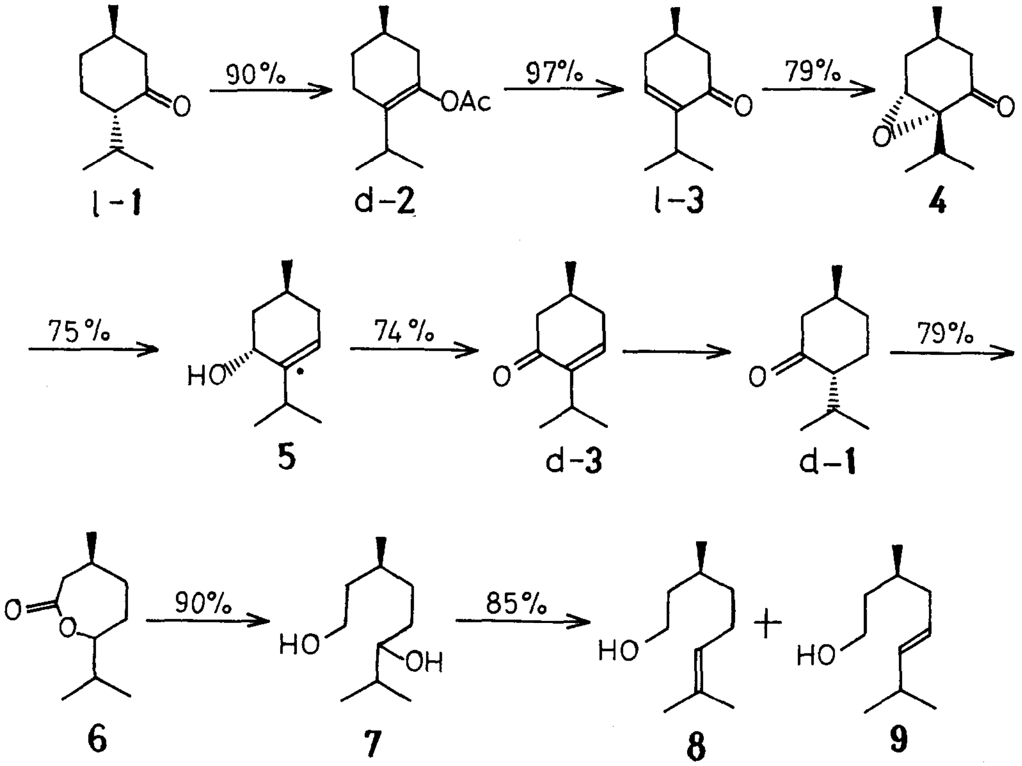
The synthetic method[1)] involving hydroalumination of optical active 3,7-dimethyl-1,6-octadiene as a key step is the only practical one to prepare l-citronellol, although d-citronellol is readily obtainable from d-citronellal[2)], and dl-citronellol from geraniol and citral[3)]. Moreover, l-menthone (l-**1**), which may be considered to be a suitable precursor of citronellol, is connected with dextrorotatory citronellol. Thus, the conversion of l-**1** to its d-isomer is essential to accomplish the preparation of l-citronellol from l-**1**. The almost quantitative formation of menthenone (**3**) from the anodic oxidation of menthenyl acetate (**2**), which has been conclusively established in our previous study[4)], may suggest the potentiality of the anodic method in the conversion of l-**1** to d-**1**.

In the present paper, we wish to report a novel synthetic method of l-citronellol from l-menthone involving the anodic transformation of **2** to **3** as one of the key steps. Scheme I illustrates the synthetic route and yields in each step.

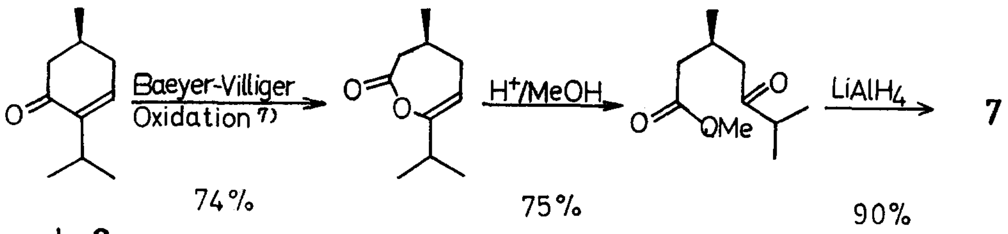
The anodic oxidation of **2**, prepared by esterification of **1**, in acetic acid containing tetraethylammonium p-toluenesulfonate as a supporting electrolyte gave l-**3** after 2.5 F/mol of electricity was passed.

Scheme I



The epoxy ketone (4), formed bv the treatment of l-3 with 30% H_2O_2 under basic condition5), could be easily reduced to the corresponding enol (5) by stirring with 100% hydrazine hydrate followed by the addition of a small amount of acetic acid at 0°. The oxidation of 5 with Jones reagent6) in acetone yielded d-menthenone (d-3), which was then hydrogenated to d-menthone (d-1) under atmospheric pressure using palladium-charcoal. The Baeyer-Villiger oxidation7) of d-1 resulted in the exclusive formation of the lactone (6), and 6 gave the corresponding diol (7) upon reduction with lithium aluminium hydride. The diol 7 could also be prepared by another route shown in scheme II.

Scheme II



d-**3**

When **7** was treated with potassium bisulfate, l-citronellol (**8**) and its isomer (**9**) were obtained in 60% and 25% yields respectively. The overall optical yield of **8** was quantitative. Physical property and optical purity of products are summarized in Table I.

Table I. Physical Property and Optical Purity of **1**-**8**.

	b.p (°C/mm)	$[\alpha]_D$ (temp. °C)	$[\alpha]_D$ (temp. °C)$^{\text{Lit.}}$
l-**1**	118/41	-17 (20°) [57.5%]$^{a)}$	-29.6 (20°)$^{8)}$
d-**2**	73/4	-63.0 (31°)	+64～+69$^{9)}$
l-**3**	77/10	-67.2 (31°)	-78.4 (16°)$^{8)}$
4	50/0.1	+59.1 (31°)	
5	70/3	+153	+165 (25°)$^{10)}$
d-**3**	98/22	+67.2 (26°)	
6	109/4	+19.2 (25°)	
7	114/2.5	+11.3 (25°)	
8	118/29	-3.11 (20°) [114%]$^{b)}$	-4.76 (20°)$^{1)}$

a) The optical purity of l-**1**.

b) The optical yield of **8**; It is almost 100% if evaluated on the basis of the reported value$^{1)}$ of the specific rotation of d-form, $[\alpha]_D^{20}$ +5.22°.

References

1) R. Rienacker and G. Ohloff, *Angew. Chem.*, *73,* 240 (1961)

2) H. E. Eschinazi, *J. Org. Chem.*, *26,* 3072 (1961).

3) R. Adams and B. S. Garvey , *J. Amer. Chem. Soc.*, *48,* 477 (1926)

4) T. Shono, Y. Matsumura and Y. Nakagawa, to be published.

5) R. L. Wasson, H. O. House, *Org. Syn.* Col. Vol. *4,* 552 (1963).

6) C. Djerassi, R. R. Engle, A. Bowers, *J. Org. Chem.*, *21,* 1547 (1956).

7) A. Baeyer and V. Villiger, *Ber.*, *32,* 3625 (1899).

8) R. Read and G. J. Robertson, *J. Chem. Soc.*, *1926,* 2209.

9) H. Schmidt, *Ann. Rept. Essent. Oils, Synthesis Perfumes*, *1938,* 124. *Chem. Abstr.* *33,*3331.

10) D. Malcolm and J. Road, *J. Chem. Soc.*, *1939,* 1037.