

# A Simple Synthesis of 9-Ketodihydro- $\alpha$ -damascone

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The compounds, 9-keto-8,9-dihydro-damascones or damascenones, are used as the ingredients in the production of perfumes and aromas.<sup>1,2</sup> Since these compounds are able to be converted into damascones and damascenones,<sup>2,3</sup> 9-keto-8,9-dihydro- $\alpha$ -damascone [2,6,6-trimethyl-1-(1,3-dioxobutyl)cyclohex-2-ene] (I) may be considered as a precursor of  $\alpha$ -damascone. Until now, (I) and its analogues were synthesized by the multistep reactions.<sup>4,5</sup>

The authors synthesized (I) by a simple reaction of  $\alpha$ -cyclogeranoyl chloride (II) and the carbanion (III) which was prepared from acetone with base.

(II) was prepared from  $\alpha$ -cyclogeranoic acid by the action of thionyl chloride (bp 43-45°C/0.4 mm Hg, 81% yield).<sup>6</sup>

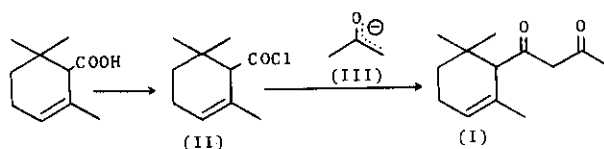
The reaction procedure was as follows: Sodium amide (15 mmol) was suspended in ether (10 ml) and refluxed for 30 minutes under nitrogen. Into this suspension, acetone (8.6 mmol) was dropped at room temperature with stirring. After 20 minutes, (II) (2.7 mmol) in dry ether (1.5 ml) was added at once to the mixture at 0°C and stirred vigorously for 5 minutes, and for 15 minutes at 20°C. Then the reaction mixture was poured into ice water and extracted with ether. Column chromatography (silica gel/benzene) of the extract gave (I) (1.07 mmol). The spectroscopic data agreed with those in the literature.<sup>4,5</sup> The aqueous layer was acidified with phosphoric acid, and  $\alpha$ -cyclogeranoic acid was recovered (1.4 mmol).

When sodium ethoxide was used as the base,

ethyl  $\alpha$ -cyclogeranoate was obtained solely. When metallic sodium was used as the base, (I) was obtained in 40% yield. In this case, however, isopropyl  $\alpha$ -cyclogeranoate was also produced in 45%, and the acid was recovered in 15%.

If the reaction was carried out at a high temperature or for a long period, the undesired aldol condensation product of acetone was produced.

1- $\alpha$ -Cyclogeranoic acid ( $[\alpha]_D^{20} -393.5^\circ$  c=0.160 ethanol)<sup>7</sup> was used as a starting substrate, then 1-(I) ( $[\alpha]_D^{20} -258.4^\circ$  c=0.237 ethanol) was obtained.



## References

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