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NEW SYNTHESIS OF γ-DAMASCONE

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γ-Damascone was selectively synthesized in good yield from γ-damascol by the oxidation of its alkoxymagnesium bromide with 1,1'-azodicarbonyldipiperidine. γ-Damascol was prepared by the reaction of γ-cyclocitral with 1-propynyllithium and the successive reduction with lithium aluminum hydride.

In the preceding paper, we reported the efficient method for preparation of γ-cyclocitral from 3-methyl-2-cyclohexenone, and γ-ionone was selectively synthesized by using γ-cyclocitral as the intermediate.1)

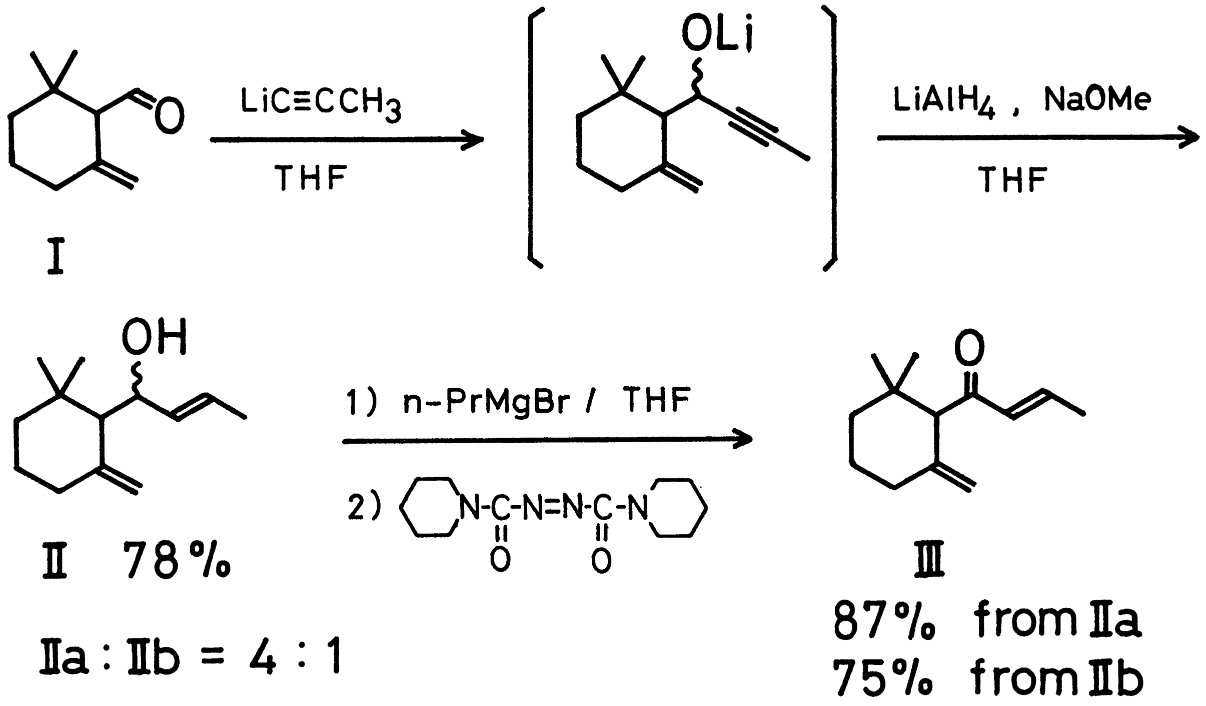
In this communication, we wish to report the selective synthesis of γ-damascone from the same intermediate, γ-cyclocitral, by employing a new method for the oxidation of alcohols2) in the key step. Concerning the synthesis of γ-damascone, several methods have been reported,3) but in these methods, it is rather difficult to synthesize γ-damascone selectively starting from readily available materials and the synthetic route from γ-cyclocitral has not been developed.

γ-Cyclocitral, the starting material in the present synthetic route, was prepared in five steps from 3-methyl-2-cyclohexenone in 35% overall yield according to the preparative method reported in the preceding paper.1)

The reaction of γ-cyclocitral (I) with 1-propynyllithium in THF for 0.5 hr at -78°C, followed by reduction with lithium aluminum hydride in the presence of sodium methoxide for 3 hr at refluxing temperature, gave mixture of two stereoisomeric alcohols, γ-damascol (IIa)4) and (IIb)5), in 78% total yield. The ratio of IIa to IIb was determined to be about 4:1 after separation by column chromatography (silica gel).

The alkoxymagnesium bromides, formed by the treatment of IIa and IIb with propylmagnesium bromide in THF at room temperature, were oxidized with 1,1'-azodicarbonyldipiperidine2) in THF at room temperature for 12 hr to give the desired γ-damascone (III) in 87% and 75% yields, respectively, without the contamination of α- and β-isomers. The structure of γ-damascone (III) was determined based on the spectral data; [III: IR (neat) 1690, 1660, 1620, 960, and 890 cm^{-1}; NMR (CCl_4) δ=0.90 (3H, s), 0.93 (3H, s), 1.84 (3H, dd, J=6.5 and 1.4 Hz), 1.0-2.4 (6H, m), 3.11 (1H, broad s), 4.65 (1H, m), 4.78 (1H, m), 6.12 (1H, dm, J=15.3 Hz), and 6.59 (1H, dq, J=15.3 and 6.5 Hz); MS (70 eV), m/e, 192 (M^+), 117, and 69].

Thus, a convenient method for the synthesis of γ-damascone is depicted below.



References and Notes

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1) T. Mukaiyama, K. Saigo, and O. Takazawa, Chem. Lett., 1976, 1033.

2) K. Narasaka, A. Morikawa, K. Saigo, and T. Mukaiyama, Bull. Chem. Soc. Jpn., submitted for publication.

3) K. H. Schulte-Elte, V. Rautenstrauch, and G. Ohloff, Helv. Chim. Acta, 54, 1805 (1971); K. H. Schulte-Elte, B. L. Müller, and G. Ohloff, Helv. Chim. Acta, 56, 310 (1973); F. Näf and R. Decorzant, Helv. Chim. Acta, 57, 1317 (1974).

4) IIa: IR (neat) 3450, 1635, 960, and 890 cm^{-1}; NMR (CCl_4) δ=0.90 (3H, s), 1.15 (3H, s), 1.70 (3H, m), 1.1-2.4 (8H, m), 4.30 (1H, m), 4.55 (1H, m), 4.85 (1H, m), and 5.55 (2H, m); MS (70 eV), m/e, 194 (M^+), 176, 124, 109, and 71.

5) IIb: IR (neat) 3400, 1640, 960, and 890 cm^{-1}; NMR (CCl_4) δ=0.90 (3H, s), 1.05 (3H, s), 1.65 (3H, m), 1.1-2.4 (8H, m), 4.15 (1H, m), 4.63 (1H, m), 4.73 (1H, m), and 5.50 (2H, m); MS (70 eV), m/e, 194 (M^+), 176, 124, 109, and 71.

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