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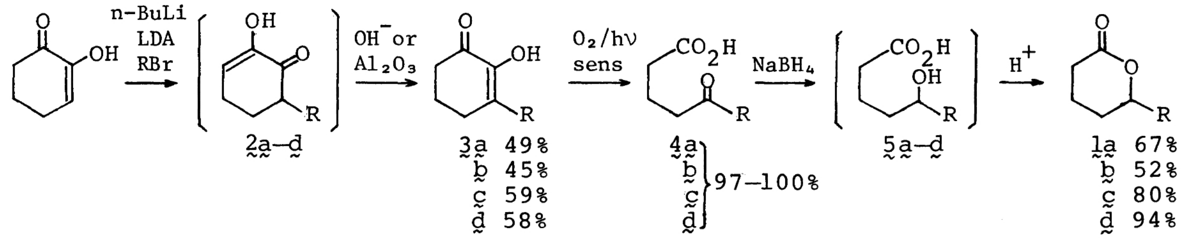
# NEW SYNTHESIS OF JASMINE LACTONE AND RELATED δ-LACTONES FROM 3-SUBSTITUTED 1,2-CYCLOHEXANEDIONES BY USE OF DYE-SENSITIZED PHOTOOXYGENATION

Masanori UTAKA, Hidesuke KURIKI, Takashi SAKAI, and Akira TAKEDA*
Department of Synthetic Chemistry, School of Engineering
Okayama University, Tsushima, Okayama 700

A new synthesis of jasmine lactone and related δ-lactones is described which uses a novel dye-sensitized photooxygenation of 3-(2-alkenyl)- or 3-(2-alkynyl)-1,2-cyclohexanediones as a key step.

Jasmine lactone (1b), a fragrant component of jasmine oil (*Jasminum grandiflorum* L.),[1)] was first synthesized in 1962 using cyclopentanone as the starting material.[2)] Since then, the method has been modified and extended mainly to carry out the oxidative lactonization of the cyclopentanone ring effectively in the presence of a labile unsaturated side chain,[3)] although an alternative method using a straight-chain sulfone acetal has also appeared.[4)] Here we report a new approach to the synthesis of jasmine lactone and related δ-lactones, which applies a dye-sensitized photooxygenation of 1,2-cyclohexanediones reported in our recent paper.[5)] Our route to the lactones using the oxygenation as a key step is shown below.[6)]



a: R = $CH_3CH_2C{\equiv}CCH_2$
b: R = *cis*-$CH_3CH_2CH{=}CHCH_2$
c: R = *trans*-$CH_3CH_2CH{=}CHCH_2$
d: R = $CH_2{=}CHCH_2$

1,2-Cyclohexanedione[7)] (1.12 g, 10.0 mmol) was made to react with 2-pentynyl bromide (4 equiv.) at -50 °C for 10 h in tetrahydrofuran after generation of its dianion at -10 °C (30 min) by addition of diisopropylamine (2.2 equiv.) and *n*-butyllithium (2.2 equiv.).[8)] The crude product (2.2 g) contained 2a as a main product. In order to isomerize 2a to 3a, it was dissolved in 130 ml of ether and stirred at room temperature for 6 h with aluminum oxide (Merck 150 Type T, 13 g).[9] Purification through a silica gel column [Wako C300, 45 g, acetone–hexane (1:20)] gave **3a** (868 mg, 49%) as a colorless oil.[10] A solution of **3a** (100 mg, 0.561 mmol) in 10 ml of methanol was irradiated at 5 °C by a 100-W tungsten-halogen lamp under oxygen with methylene blue (3 mg) as a sensitizer.[5] The oxygenation was completed after 3 h, accompanied by absorption and evolution of oxygen and carbon monoxide, respectively. The methanol was evaporated and the residual blue oil was dissolved in ether. The heterogeneous solution was filtered and evaporated to give almost pure **4a** (102 mg, 100%) as a pale yellow oil. Reduction of **4a** to **5a** with sodium borohydride in aq sodium hydrogen carbonate and subsequent lactonization of **5a** by refluxing in benzene with *p*-toluenesulfonic acid gave **1a** in 67% yield after purification by preparative TLC. Finally, the lactone **1a** was hydrogenated using Lindlar catalyst[11] to afford **1b** (90%) as a colorless oil. The $^{1}$H NMR spectrum was identical with that reported by Kondo et al.[4] and the IR spectrum was completely identical with that reported for the natural product.[2]

The lactone obtained through the intermediates **2b** to **5b** was an 83:17 mixture of **1b** and **1c**, because *cis*-2-pentenyl bromide prepared by bromination of *cis*-2-penten-1-ol[12] was inevitably contaminated with the trans isomer.

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## References

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6) The yields given are for isolated products.
7) Prepared conveniently from 2,6-dibromocyclohexanone according to the method described in M. Utaka, S. Matsushita, and A. Takeda, *Chem. Lett.*, **1980**, 779.
8) We have modified the method reported by A. S. Kende and R. G. Eilerman, *Tetrahedron Lett.*, **1973**, 697.
9) Compounds **2b**–**d** were isomerized to **3b**–**d** by hydroxide-ion catalysis but **2a** was found to be vulnerable to alkali. We have found that aluminum oxide is a good catalyst for the isomerization.
10) Satisfactory spectral data (IR and NMR) were obtained for **1a**–**d** to **5a**–**d**.
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