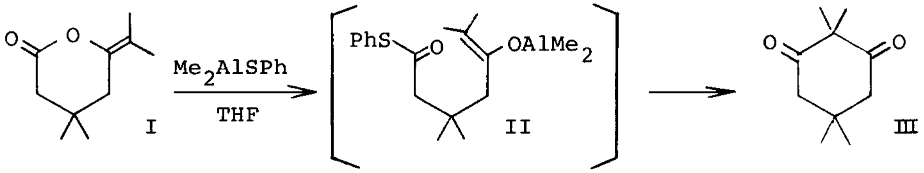
Tetrahedron Letters,Vol.23,No.1,pp 99-100,1982 0040-4039/82/010099-02$03.00/0
Printed in Great Britain

# ORGANOALUMINIUM REAGENTS INDUCED ISOMERIZATION OF 5-HYDROXY-3,3,6-TRIMETHYL-5-HEPTENOIC ACID δ-LACTONE TO 2,2,5,5-TETRAMETHYL-1,3-CYCLOHEXANEDIONE

Hiroki Tomioka, Koichiro Oshima,* and Hitosi Nozaki
Department of Industrial Chemistry, Faculty of Engineering,
Kyoto University, Yoshida, Kyoto 606, Japan

*Abstract: Treatment of the title lactone and the related δ or ε-lactones with $Et_2AlSR$ (R = Et or Ph) gave 1,3-cyclohexanediones or 1,3-cycloheptanediones in excellent yields.*

Organoaluminium compounds are attractive reagents for aldol type condensation.[1] Although methods are available for converting a carbonyl compound into a reactive aluminium enolate, there still exists a need for new methods effecting complicated synthesis. Here we describe a new process for the transformation of an olefinic lactone into a 1,3-diketone via a probable intermediate, the aluminium enolate II.

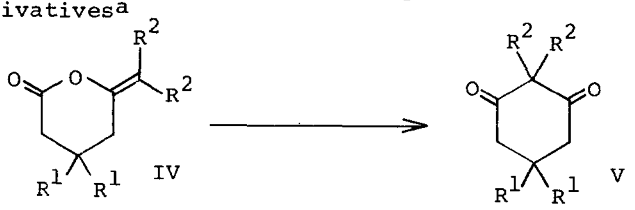


A solution of PhSH (0.24 g, 2.2 mmol) in hexane (10 ml) was added to a solution of trimethylaluminium in hexane (1.0*M*, 2.2 ml, 2.2 mmol) at 0°C under argon atmosphere. After stirring for 30 min at 0°C, the solvent was removed *in vacuo* to leave a white solid $Me_2AlSPh$.[2] A solution of δ-lactone I (0.34 g, 2.0 mmol) in tetrahydrofuran[3] (15 ml) was added and the resulting mixture was heated at reflux for 1 h. Dilution with ether (20 ml), acidic workup, and final purification by silica gel column chromatography gave the 1,3-diketone III (0.31 g, 91% yield).

Dimethylaluminium ethanethiolate and $Me_2AlSeMe$ were also effective for the transformation (yield of III, 97% and 89%, respectively). Magnesium benzenethiolate (IMgSPh) and LiSPh were less effective as far as the yields of III are concerned (72% and 27%).[4]

Lactones IV in Table 1 were prepared by the previously reported photo-reaction[5] and the combination of this new method and photo process

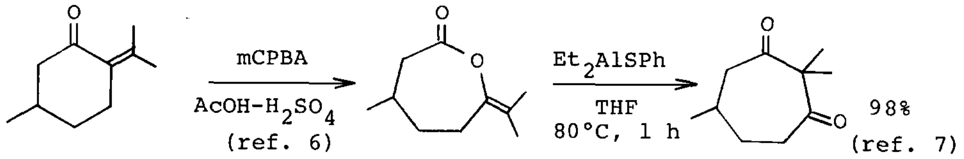
Table 1. Isomerization of 5-hydroxy-5-heptenoic acid δ-lactone derivatives[a]



| Run | Substrate $R^1$ | Substrate $R^2$ | Reaction Time (h) | Yield of 1,3-Diketone(%) |
|---|---|---|---|---|
| 1 | Me | Me | 1 | 91 |
| 2 | H | $-(CH_2)_4-$ | 0.5 | 83 |
| 3 | Me | $-(CH_2)_4-$ | 1 | 85 |
| 4 | Me | $-(CH_2)_5-$ | 1 | 93 |

[a] Reactions were performed on 2.0 mmol scale in THF at 80°C.

accomplished the cycle V ⟶ IV ⟶ V. Simple synthetic application of the new method to 1,3-cycloheptanedione from pulegone is shown below.[8]



## References and Notes

1. (a) A. Itoh, S. Ozawa, K. Oshima, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, 54, 274 (1981) and references cited therein. (b) J. Tsuji, T. Yamada, M. Kaito, and T. Mandai, *Tetrahedron Lett.*, 1979, 2257.
2. N. Davidson and H. C. Brown, *J. Am. Chem. Soc.*, 64, 316 (1942).
3. Tetrahydrofuran was found to be the best solvent for the aldol type reaction of aluminium enolates. See ref. 1.
4. Unidentified polar by-products were formed in the case of LiSPh.
5. H. Nozaki, Z. Yamaguti, and R. Noyori, *Tetrahedron Lett.*, 1965, 37.
6. J. L. Marshall, J. P. Brooks, and G. W. Hatzenbuehler,III, *J. Org. Chem.*, 34, 4193 (1969).
7. Mp. 53-55°C; IR ($CCl_4$) 1700, 1460, 1380, 1108 $cm^{-1}$; NMR ($CDCl_3$) δ1.23 (s, 6H), 1.00 (d, 3H, J = 6.3 Hz). W. Reusch, D. F. Anderson, and C. K. Johnson, *J. Am. Chem. Soc.*, 90, 4988 (1968).
8. Financial support by the Ministry of Education, Science, and Culture, Japanese Government (Grant-in-Aid #56430027), is acknowledged.

(Received in Japan 19 September 1981)