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A Novel Synthesis of Lactones by the Oxidation of Alicyclic Ketones with Oxone in Aprotic Solvent in the Presence of "Wet-Alumina"

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Oxidation of cycloalkanones with Oxone in dichloromethane in the presence of "wet-alumina" afforded lactones in good yield under mild conditions.

Lactones occur in nature and are also important intermediates in organic synthesis. Thus, a great number of types of reactions have been developed for lactone syntheses.[1] In this article, we wish to present an alternative approach for lactone synthesis by using the title oxidation.

The following procedures are representative. "Wet-alumina" was prepared by vigorous shaking of commercial super-dried Alumina A (Super I; 20 g) with distilled water (4 g) untill a free-flowing powder was obtained (It should be done in a few min). To a heterogeneous mixture of Oxone (1)[2] (2.5 moles of ketone) and "wet-alumina" (2 g) in dichloromethane (DM; 10 cm^3) in a round-bottomed flask was added 2 (0.3 g) in one portion. The flask was flushed with dry argon to exclude any influence of autoxidation and then capped tightly with a glass stopper. After magnetic stirring for 24 h under reflux, the cooled mixture was filtered through a sintered glass disk and the residue was thoroughly washed with DM or dry ether. Removing the combined filtrate *in vacuo* left 3, which was slightly contaminated with the parent ketone and thus immediately chromatographed on silica gel eluted with DM. Thus, this system can be treated just like a supported reagent consisting of alumina and an oxidant,[3] except that the present oxidation is instantly performable without operationally laborious preparation of a supported reagent. It should be noted that sufficiently efficient stirring is indispensable to attain smooth and reproducible reaction.

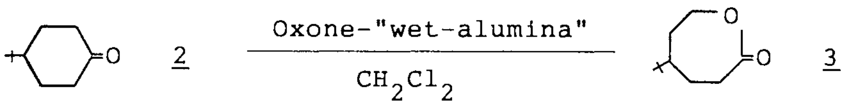
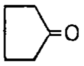
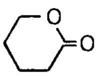
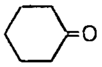
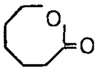
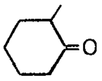
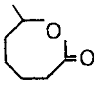
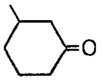
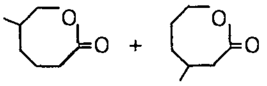
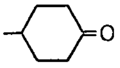
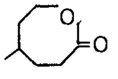
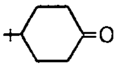
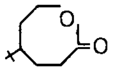
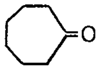
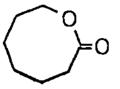


Table 1 gives the results obtained under comparable conditions; some differences in reaction times were mainly ascribed to the differences in reactivity of the ketones. Lactone yields in Entries 1-2 were found to be much superior to those given under aqueous conditions.[4] This system can also be applied to a larger-membered ketone (Entry 7), albeit in low yield.

Table 1. Oxidation of Alicyclic Ketones with Oxone (1)[a]

Entry No.	Ketones	Time/h	Lactones	Isolated yield/%	
1		24		80	
2		8		79	
3		20		79	
4		20		85	(6:4 by NMR)
5		20		80	
6		24		80	
7		24		23	

a) Under argon, reflux; 0.3 g of ketone, 2 g of "wet-alumina", and 10 cm^3 of CH_2Cl_2 were used; [1]/[Ketone]= 2.5 (mole ratio).

In summary, a number of lactones have been effectively prepared from cycloalkanones by means of a combination of 1 and "wet-alumina" in DM under mild conditions. The oxidative property of 1 is intimately analogous to conventional peracids[5] and thus the present procedures constitute a novel Baeyer-Villiger-type reaction characterized by manipulative simplicity.

References

1)Methods for lactone synthesis have been briefly reviewed in "Shin-Jikken Kagaku Kouza," Vol. 14, II , p. 1062-1099. 2)Oxone is a stable composite of $KHSO_5$, $KHSO_4$, and K_2SO_4 in 2:1:1 molar ratio and is available from Aldrich Chemical Co. 3)A. Mckillop and D. W. Young, Synthesis, 1979, 401, 481; G. H. Posner, Angew. Chem., Int. Ed. Engl., 17, 487 (1978); G. H. Posner, "Preparative Chemistry Using Supported Reagents," ed by P. Laszlo, Academic Press, Inc., San Diego (1987), p.287. 4)R. J. Kennedy and A. M. Stock, J. Org. Chem., 25, 1901 (1960). 5)C. H. Hassall, Org. React., 9, 73 (1957).

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