Tetrahedron Letters, Vol.22, No.27, pp 2595 - 2598, 1981
Printed in Great Britain

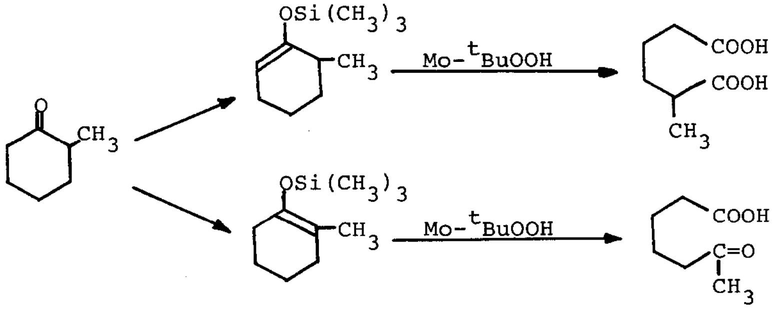
0040-4039/81/272595-04$02.00/0

DOUBLE BOND CLEAVAGE REACTION OF SILYL ENOL ETHERS USING $MoO_2(acac)_2$ -^tBuOOH

Kiyotomi Kaneda, Nobuyoshi Kii, Koichiro Jitsukawa, and
Shiichiro Teranishi
Department of Chemical Engineering, Faculty of Engineering Science,
Osaka University, Toyonaka, Osaka 560, Japan

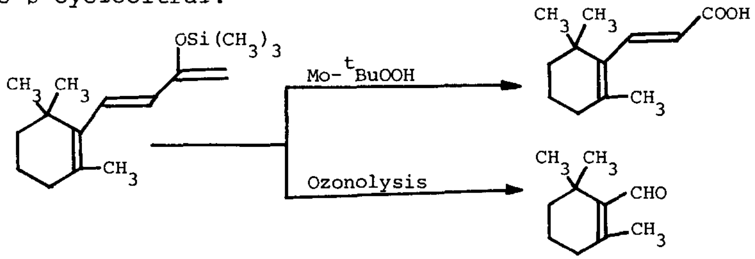
Abstract: The double bond of various silyl enol ethers is smoothly cleaved to give carbonyl compounds by an oxidizing reagent $MoO_2(acac)_2$-^tBuOOH.

Previously we have reported that the oxygenation of enamines in the presence of Cu catalysts gave double bond cleavage compounds.[1] A mechanism involving a ternary complex of O_2, enamine, and Cu was proposed on the basis of the ionization potential of enamines and kinetic study. In the course of studying the double bond cleavage oxidation of electron rich olefins using metal catalysts, we now find that the double bond of silyl enol ethers is smoothly cleaved to give the corresponding carbonyl compounds by an oxidizing reagent $MoO_2(acac)_2$ -^tBuOOH. Considering regiospecific generation of silyl enol ethers can be easily achieved under conditions of either kinetic or thermodynamical control,[2] the reaction is a powerful method for regiospecific α-cleavage of ketonic precursors.[3] This oxidizing reagent can compete in convenient with the ozonolysis technic.[4,5]



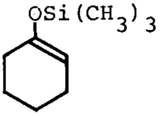
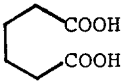
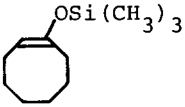
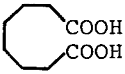
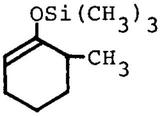
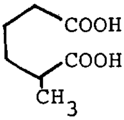
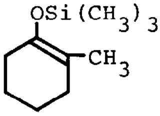
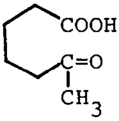
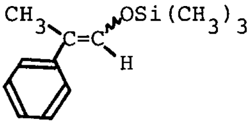
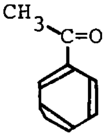
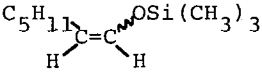
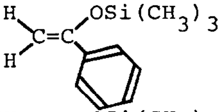
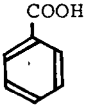
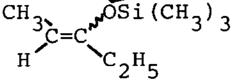
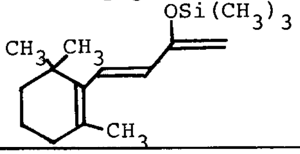
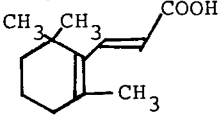
The typical experimental procedure is exemplified by the reaction of trimethylsilyl enol ether of cyclohexanone(run 1). $MoO_2(acac)_2$(0.01 g, 0.03 mmol) and the silyl ether(0.51 g, 3 mmol) was dissolved in anhydrous benzene(8 ml) under a nitrogen atmosphere and a solution of ^tBuOOH(1.35 g, 12 mmol) in anhydrous benzene(12 ml) was dropwised. The solution was stirred at 60°C for 48 h. A mixed solution of CF_3COOH-THF-H_2O(3:1:1, 20 ml) was then added. The mixture was further stirred at 60°C. Adipic acid crystals separated from the resulting mixture, and after 24 h they were collected, washed with benzene, and dried, weight 0.377 g(86%).

Some examples of the oxidation are shown in Table. Various kinds of silyl enol ether of ketones and aldehydes easily reacted with the reagent $MoO_2(acac)_2$ -^tBuOOH. Mono- and dicarboxylic acids as cleavage products are formed in almost quantitative yields. Exceptional are β-disubstituted silyl enol ethers (run 4, 5), which gave ketocarboxylic acid and ketone compounds. In the case of the silyl ether of β-ionone(run 9), the double bond with the trimethylsilyloxy group was selectively cleaved to give β-(2,6,6-trimethylcyclohexenyl)acrylic acid. This high regioselectivity is a sharp contrast to that with the ozonolysis which gives β-cyclocitral.[4]



The mechanism of this oxidation is presently unclear, although the epoxide may be the initial formed intermediate: α-trimethylsilyloxyketone derived from the rearrangement of the epoxide[4,6] could be detected when using an equimolar amount of ^tBuOOH to the silyl enol ether of cyclohexanone and the isolated α-silyloxyketone gave adipic acid under oxidation conditions using $MoO_2(acac)_2$ -^tBuOOH(60°C, 24 h).

Table. Oxidation of Silyl Enol Ethers with $MoO_2(acac)_2$-^tBuOOH[a]

Run	Silyl Ether	Product[b]	Yield(%)[c]
1			86[d]
2			86[d]
3			90[d]
4			90
5			98
6		$C_5H_{11}COOH$	95[e]
7			92
8		C_2H_5COOH CH_3COOH	93[e] 93[e]
9			85[d]

---

[a] Oxidation was performed at 60°C for 48 h in benzene(20 ml) containing silyl enol ether(3 mmol), t-BuOOH(12 mmol), and $MoO_2(acac)_2$(0.03 mmol).

[b] All products were identified by ^{1}HNMR and IR spectra. [c] Determined by GLPC

[d] Isolated yield. [e] These products contain about 10% corresponding trimethysilyl esters.

Acknowledgement: This work was supported in part by a Grant-in-Aid(No 555323) for Scientific Research from the Ministry of Education of Japan, which is greatful acknowledged.

References and Notes

(1) a) T. Itoh, K. Kaneda, T. Watanabe, S. Ikeda, and S. Teranishi, Chem. Lett., 227 (1976). b) Similar oxygenation also occurred in the case of cyclopropylamines having quasi-double bond character of cyclopropane ring. See: T. Itoh, K. Kaneda, and S. Teranishi, Tetrahedron Lett., 2809 (1975).

(2) See for reviews a) E. W. Colvin, Chemical Society Reviews, 7, 15 (1978). b) I. Fleming, "Comprehensive Organic Chemistry. The synthesis and Reactions of Organic Compounds", Vol. 3, D. Neville Jones, Ed., Pergamon Press, Oxford, 1979, p 541.

(3) Hudrlik reported that Baeyer-Villiger reaction of β-trimethylsilylketones were directed by the trimethylsilyl group to give esters of β-hydroxysilanes. See: P. F. Hudrlik , A. M. Hudrlik, G. Nagendrappa, T. Yimenu, E. T. Zellers, and E. Chin, J. Am. Chem, Soc., 102, 6894 (1980).

(4) R. D. Clark and C. H. Heathcock, J. Org. Chem., 41, 1396 (1976).

(5) Other epoxidizing reagents were tested for this oxidation. But the reaction with m-CPBA did not afforded high selectivity for the cleavage products and $VO(acac)_2$-^tBuOOH showed no catalytic activity.

(6) G. M. Rubottom, M. A. Vazquez, and D. R. Pelegrina, Tetrahedron Lett., 4319 (1974).

(Received in Japan 31 March 1981)