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PERACID-INDUCED OXIDATION OF 2,5-DISUBSTITUTED FURANS TO CIS-1,2-DIACYLETHYLENES

Yuichi KOBAYASHI, Harutaka KATSUNO, and Fumie SATO*
Department of Chemical Engineering, Tokyo Institute of Technology,
Meguro-ku, Tokyo 152

2,5-Disubstituted furans are oxidatively cleaved by peracids to cis-1,2-diacylethylenes in high yields under mild conditions.

cis-1,2-Diacylethylenes are valuable intermediates for syntheses of prostagrandins$^{1)}$ and rethrolones.$^{2)}$ Considerable attention has been paid to the syntheses of these compounds by oxidative ring cleavage of 2,5-disubstituted furans.$^{3)}$ The methods that have been used successfully include bromine-induced oxidation,$^{3)}$ electrochemical oxidation,$^{4)}$ photosensitized oxygenation,$^{5)}$ hydrogen peroxide oxidation,$^{6)}$ pyridinium chlorochromate oxidation,$^{7)}$ sodium hypochlorite oxidation,$^{8)}$ and tert-butylhydroperoxide oxidation catalyzed by $VO(acac)_2$.$^{9)}$ Although these techniques possess variable degrees of utility, many of these methods suffer some disadvantages such as contamination of undesired trans-isomers, necessity of an additional step after oxidation, lack of generality and/or requirement of special equipments.

Peracids are powerful oxidizing agents and are widely and commonly used for oxidation of various organic substrates including furans.$^{10)}$ To the best of our knowledge, however, no example of oxidation of 2,5-disubstituted furans **1** to cis-1,2-diacylethylenes **2** have been reported.$^{11)}$ We report here the successful conversion of 2,5-disubstituted furans **1** to cis-1,2-diacylethylenes **2** by m-chloroperbenzoic acid or peracetic acid. The results are summarized in Table 1.

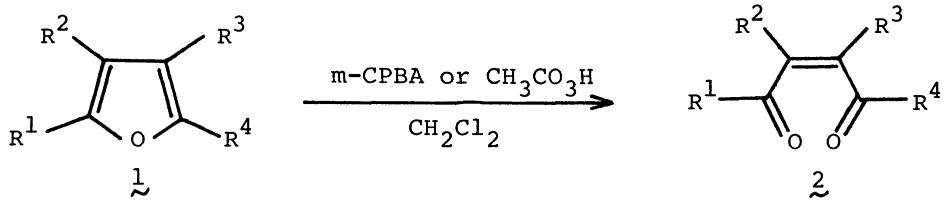


Table 1. Oxidation of Furans by Peracids[a)]

Run	Furan 1	R^1	R^2	R^3	R^4	Peracid[b)]	Yield/% of product 2
1	1a	CH_3	H	H	n-C_6H_{13}	m-CPBA	86
2	1a	"	"	"	"	CH_3CO_3H	58
3	1b	n-C_4H_9	"	"	n-C_4H_9	m-CPBA	87
4	1c	CH_3	$SiMe_3$	"	C_2H_5	CH_3CO_3H	70
5	1d	n-C_3H_7	"	"	"	"	79
6	1e	"	"	"	i-C_3H_7	"	78[c)]
7	1f	"	"	"	Ph	"	91

a) All reactions were carried out in CH_2Cl_2 at 0-7 °C for 1 h.

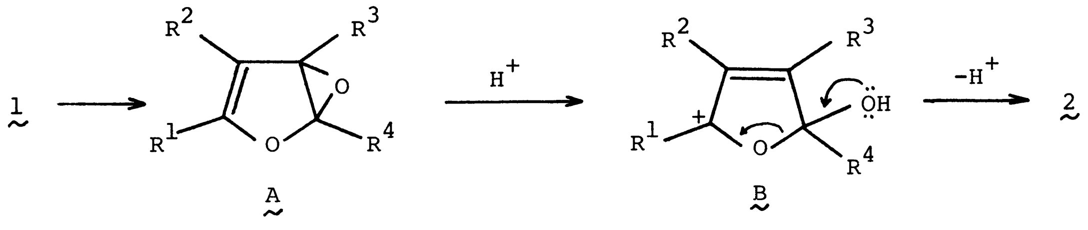
b) Commercially available 80% m-CPBA and 40% CH_3CO_3H were used.

c) Use of m-CPBA instead of CH_3CO_3H reduced the product yield.

It is clear from Table 1 that 2,5-disubstituted furans 1 are readily oxidized to the corresponding cis-1,2-diacylethylenes 2 in high yields under mild conditions.[12)] The products 2 possess a cis relationship and are not contaminated by trans-isomers.[13)] As the furans 1 possessing trimethylsilyl group at C-3 can be readily prepared from 3-trimethylsilylprop-2-yn-1-ols via hydromagnesiation,[14)] the present reaction offers a convenient way to 1,2-diacylvinylsilanes such as 2c-f which can serve as a useful Michael acceptor.

Mechanistically, the oxidation appears to follow the pathway shown below. Direct oxidation of furan ring by the peracid affords the intermediate A. Addition of proton on the epoxide oxygen of A followed by epoxide ring opening yields the cation B. Removal of proton from B with furan ring opening leads to 2.

Typical experimental procedures are illustrated in the oxidation of 2-hexyl-5-methylfuran (1a) and 5-ethyl-2-methyl-3-trimethylsilylfuran (1c). Run 1



(Table 1): To a solution of the furan 1a (270 mg, 1.6 mmol) in CH_2Cl_2 (4 ml) was added m-CPBA (370 mg, 1.8 mmol) at 0 °C. After 1 h at 0 °C, aqueous $Na_2S_2O_3$ solution (20 ml, 1 mol dm^{-3}) was added and the product was extracted with ether repeatedly. Evaporation of the ethereal extracts followed by chromatography of the residue on silica gel gave the product 2a (250 mg) in 86% yield. Run 4 (Table 1): To a mixture of NaOAc (70 mg, 0.85 mmol) and CH_3CO_3H (0.53 ml, 2.8 mmol) in CH_2Cl_2 (3 ml) was added a solution of the furan 1c (130 mg, 0.70 mmol) in CH_2Cl_2 (3 ml) at 7 °C. The resulting mixture was stirred at 7 °C for 1 h. Then aqueous $Na_2S_2O_3$ solution (10 ml, 1 mol dm^{-3}) and aqueous $NaHCO_3$ solution (10 ml, 1 mol dm^{-3}) was added successively. After 30 min at 25 °C, extraction and purification as described above provided the product 2c (97 mg,) in 70% yield.

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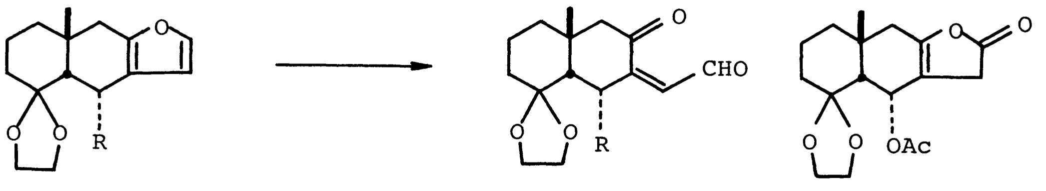
11) Recently, the oxidation of the furan 3 with m-CPBA to give the 1,4-dicarbonyl compound 4 have been reported by M. Tada in his terpene synthesis.10) However, the corresponding acetate 5 was transformed to a mixture of 6 and 7 in a ratio of 2:3.



3 R = H
5 R = Ac

4 R = H
6 R = Ac

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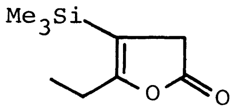
12) In the oxidation of furans in which R^4 is H the products were dependent on the substrates. Thus, 2-ethyl-3-trimethylsilylfuran gave the Δ^3-butenolide 8, (by oxidation with m-CPBA), 2-phenyl-3-trimethylsilylfuran yielded the product 9 (m-CPBA), and 2-octylfuran produced the Δ^2-butenolide 10 (CH_3CO_3H).10)



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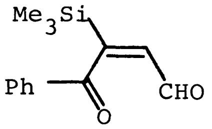

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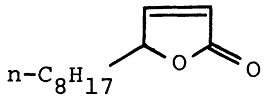

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13) cis-1,2-Diacylethylenes 2 can be readily isomerized to trans-isomers under acidic conditions.15) In fact, complete isomeization of 2b to the trans-isomer occured when 2b was treated with 3 mol dm^{-3} HCl in ether (30 min, room temperature). However, no trans-isomers were yielded (TLC and ^1H NMR) in the present reaction.

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