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REACTION OF OXIRANES WITH DIANION OF METHYL ACETOACETATE IN THE PRESENCE OF BORON TRIFLUORIDE ETHERATE

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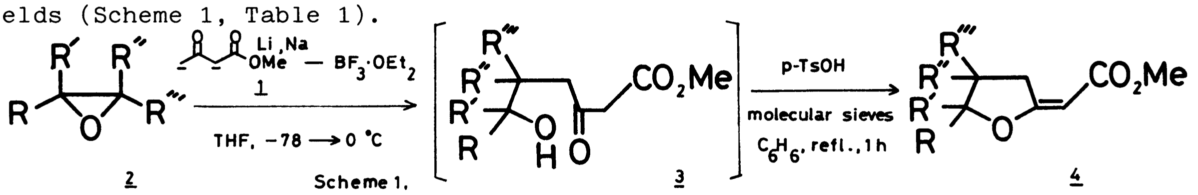
Oxiranes were reacted with dianion of methyl acetoacetate in the presence of boron trifluoride etherate to give the substituted tetrahydro-2-furylideneacetates, which were further converted to γ-lactones.

Cleavage of oxiranes with diaions of acetoacetates is a convenient method for the synthesis of oxygen containing heterocycles.1) The reaction , however, is sensitive to the steric hinderance at the oxirane carbon, and its application to the polysubstituted oxiranes often results in low yield of the products. In the present communication, we wish to describe an efficient synthesis of substituted tetrahydro-2-furylideneacetates (4), which involves the reaction of substituted oxiranes (2) with the dianion of methyl acetoacetate (1) in the presence of boron trifluoride etherate.

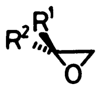
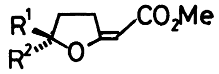
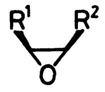
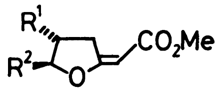
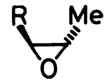
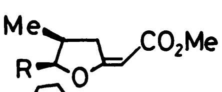
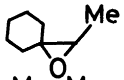
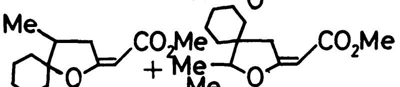
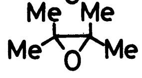
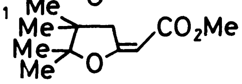
Under a nitrogen atmosphere, the dianion (1) was prepared from methyl acetoacetate (2.0 mmol), sodium hydride (2.0 mmol), and a butyllithium-hexane solution (1.3 ml, 2.0 mmol) in THF (2 ml) according to Weiler's procedure.2) Then, various substituted oxiranes (2) (0.5 mmol) in THF (2 ml) and boron trifluoride etherate (0.4 ml) was added successively at -78 °C and the mixture was warmed to 0 °C for 2 h. The resulting methyl 6-hydroxy-3-oxoalkanoates (3), without isolation, were dehydrated in the presence of molecular sieves 4A and a catalytic amount of p-toluenesulfonic acid in refluxing benzene (5 ml), and the corresponding tetrahydro-2-furylideneacetates (4) were obtained in high yields (Scheme 1, Table 1).



Scheme 1.

The presence of the Lewis acid is essential especially to the cleavage of polysubstituted oxiranes, although mono- and 1,1-disubstitutes oxiranes react with 1 without the acid catalyst at r. t. (Table 1). Also observed is that the use of 2-4 equivalents of 1 to 2 gave the products in higher yields (entry 4). In general, the substitution ocurred at the less hindered site of oxiranes (entries 1, 2, and 3), and in the case of 2,3-disubstituted oxiranes, the attack

Table 1. Synthesis of Tetrahydro-2-furylideneacetates (4)[a]

Entry	Oxirane (2)		Product (4)		Yield / %[b]
1		2a: R^1=n-C_5H_{11} R^2=H		4a	71, 77[e]
2		2b: R^1=$PhCH_2OCH_2$ R^2=Me		4b	96, (64)
3		2c: R^1=$Ph(CH_2)_3$ R^2=Me		4c	91
4		2d: $R^1,R^2=(CH_2)_4$		4d	65, (63), 40[g]
5		2e: R^1=n-C_4H_9 R^2=Me		4e[c]	63, 65[e], (-)[f]
6		2f: R=n-C_4H_9		4f[d]	60, (-)[f]
7		2g: R=i-Pr		4g	65, (trace)
8		2h		4h	87, (-)[f]
9		2i		4i	44, (-)[f]

a) The reaction was carried out using 0.5 mmol of 2 and 2.0 mmol of 1, unless otherwise noted, and the products gave satisfactory ^{1}H-NMR, IR, and/or ^{13}C-NMR spectra.

b) In parentheses are shown the yields of 4 obtained by the reaction without $BF_3 \cdot OEt_2$ at r. t. (overnight).

c) A 5:1 mixture of regioisomers was obtained, and the major isomer is shown.

d) A 8:1 mixture of regioisomers was obtained, and the major isomer is shown.

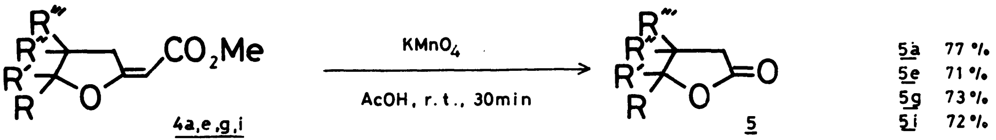
e) The reaction was carried out with 5.0 mmol of 2 and 10.0 mmol of 1.

f) The product (4) was not detected by thin layer chromatography.

g) The reaction was carried out with 1.0 mmol of 2 and 1.0 mmol of 1.

at the methyl substituted carbon predominated over the reaction at butyl or isopropyl substituted carbon (entries 5, 6, and 7). The discrimination between the secondary and tertiary carbons, however, was not successful (entry 8). The substitution took place stereospecifically, and trans- and cis-2,3-epoxyheptanes (2e and 2f) gave the cis- and trans-4,5-disubstituted tetrahydro-2-furylideneacetates (4e and 4f), respectively (entries 5 and 6).

Next, 4 was converted to γ-lactone (5) by the oxidative cleavage of the double bond with 2 molar of potassium permanganate in acetic acid at r. t. (Scheme 2). It should be noted that these processes would furnish a method for the synthesis of polysubstituted δ-lactones from oxiranes.



Scheme 2.

References
1) T. A. Bryson, J. Org. Chem., 38, 3428 (1973); G. R. Kieczykowski, M. R. Roberts, and R. H. Schlessinger, ibid., 43, 788 (1978). 2) L. Weiler, J. Am. Chem., 92, 6702 (1970).

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