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AN AROMATIC VERSION OF CLAISEN REARRANGEMENTS OF ESTER SILYL ENOLATES —— A FACILE SYNTHESIS OF 2,3-DISUBSTITUTED FURANS

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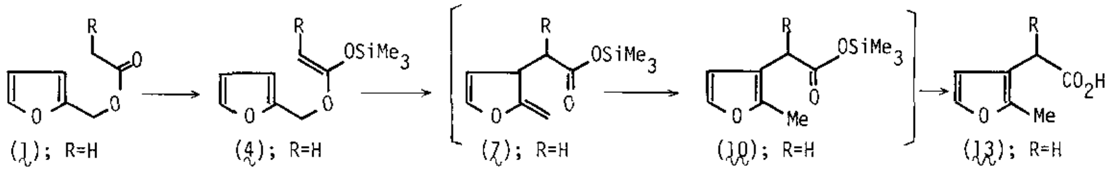
Abstract —— The [3,3]sigmatropic rearrangement of furfuryl ester silyl enolates (4)∿(6) was studied and found to proceed under very mild conditions to give the carboxylic acids (13)∿(15) after acid treatment.

The [3,3]sigmatropic rearrangement of allyl vinyl ethers, in both its aromatic and aliphatic modes, has become a cornerstone for the construction of new carbon to carbon bonds with high regio- and stereospecificity[1-3]. Recently an attention has been focussed on the Claisen rearrangement in systems where the allylic double bond of the allyl vinyl ether is formally incorporated in a heterocyclic aromatic ring[4-10] partially because of the synthetic potentials of the rearranged products for subsequent transformations. However, this type of rearrangement has required rather forcing conditions. So, we have sought rather mild conditions and investigated the feasibility and effectiveness of an aromatic variation of Ireland's allylic ester silyl enolate rearrangement[11-17].

Thus, the esters (1)[18], (2)[19], and (3)[20] were firstly converted into the silyl enolates (4∿7), respectively, in a standard manner[12,13] (LDA, TMSCl, THF, - 78 °C) and then subjected to the rearrangement [for 4, (THF, reflux, 22 h); 5, (THF, room temperature, 17 h); 6, (THF, reflux, 5 h)]. After the hydrolysis (10% HCl, THF, room temperature, 5 min) of the resulted silyl esters (10∿12), the corresponding acids (13), [m/z 140 (M^+); IR ($CHCl_3$) 1710 cm^{-1}; ^{1}HNMR (CCl_4) δ 2.18 (3H, s), 3.25 (2H, s), 6.10 (1H, d, *J* = 2 Hz), 7.05 (1H, d, *J* = 2 Hz)], (14) [m/z 154 (M^+);

IR (CCl_4) 1700 cm^{-1}; ^{1}HNMR ($CDCl_3$) δ 1.35 (3H, d, *J* = 7 Hz), 2.20 (3H, s), 2.45 (1H, q, *J* = 7 Hz), 6.08 (1H, d, *J* = 2 Hz), 7.02 (1H, d, *J* = 2 Hz)], and (15) [m/z 248 (M^+); IR ($CHCl_3$) 1720 cm^{-1}; ^{1}HNMR (CCl_4) δ 2.03 (3H, s), 4.52 (1H, s), 6.37 (1H, d, *J* = 2 Hz), 7.09 (1H, d, *J* = 2 Hz), 7.10∼7.22 (5H, m)] were obtained in 32%, 20%, and 21.7% yields, respectively. In this rearrangement, it is clear that the silyl enolates (4∼6) were initially rearranged in [3,3]sigmatropic manner to give the γ,δ-unsaturated esters (7∼9), whose hydride shift afforded the aromatised esters (10∼12), respectively.



(1); R=H
(2); R=Me
(3); R=CH_2SPh

(4); R=H
(5); R=Me
(6); R=SPh

(7); R=H
(8); R=Me
(9); R=SPh

(10); R=H
(11); R=Me
(12); R=SPh

(13); R=H
(14); R=Me
(15); R=SPh

Scheme

Thus, we could show that the aromatic version of Ireland's allylic ester silyl enolate rearrangement provides a mild and effective method for the synthesis of 2,3-disubstituted furans. Our observations were good agreement with the trend in acidic Claisen rearrangements, wherein the rate of Ireland's[13] silyl ketene acetal variation is much faster than the classical vinyl ether case[1] for comparable substitution.

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20) The compound (**3**) [m/z 248 (M^+); IR ($CHCl_3$) 1740 cm^{-1}; ^{1}HNMR ($CDCl_3$) 3.41 (2H, s), 4.92 (2H, s), 6.18 (2H, s), 6.95 (1H, s), 7.01 7.43 (5H, m) were prepared by esterification ($PhSCH_2CO_2H$, DCC, 4-DMAP, CH_2Cl_2, room temperature, 15 h) of 2-furfuryl alcohol in 86% yield.

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