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STEREOSELECTIVE SYNTHESIS OF CONTIGUOUSLY SUBSTITUTED BUTYROLACTONES BASED ON THE CYCLIC ALLYLSULFONIUM YLIDE REARRANGEMENT

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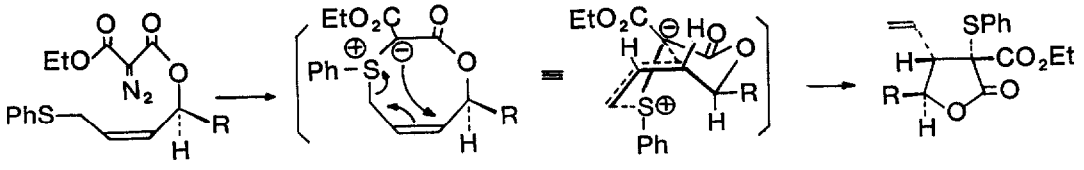
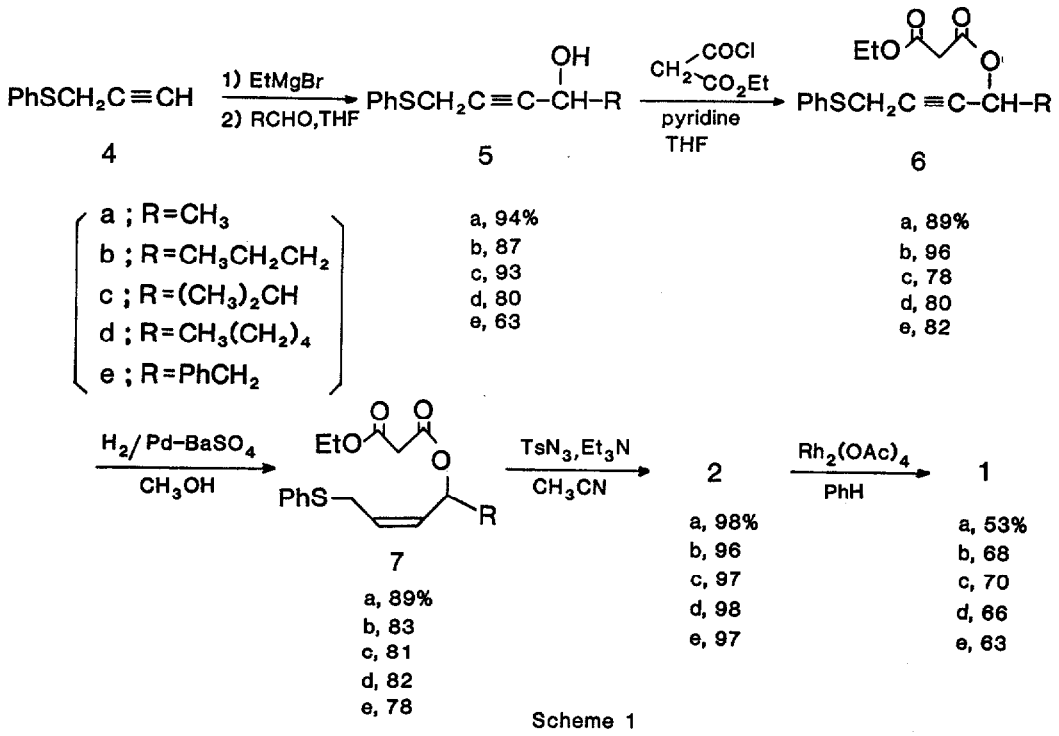
Summary: α-Diazomalonates of (Z)-4-phenylthio-2-buten-1-ol homologues (**2**) stereoselectively provided γ-alkyl-α-ethoxycarbonyl-α-phenylthio-β-vinylbutyrolactones (**1**) by the [2.3]sigmatropic rearrangement of cyclic sulfonium ylides (**3**) intramolecularly generated therefrom with rhodium acetate.

The [2.3]sigmatropic rearrangement of allylic sulfonium ylides has recently been received much attention in organic chemistry.[1] In this reaction, rhodium acetate has been found to be a catalyst that is particularly efficient for the generation of sulfonium ylides from sulfides and diazo compounds.[2] In connection with an ongoing project in this laboratory, we wish to report here the highly stereoselective synthesis of contiguously substituted γ-butyrolactones (**1**) by the [2.3]sigmatropic rearrangement of eight-membered cyclic sulfonium ylides (**3**) which were generated by intramolecular addition from diazo sulfides (**2**) in the presence of rhodium acetate.



2 **3** **3a** **1**

Z-Olefins (**2**) containing both diazo and sulfide groups were prepared from propargyl bromide by a 6-step synthetic sequence as follows (Scheme 1); treatment of phenyl propargyl sulfide (**4**),[3] readily obtainable from propargyl bromide in benzene and aqueous sodium thiophenoxide in the presence of a phase transfer catalyst (tetrabutylammonium hydroxide) in quantitative yield,[4] with ethylmagnesium bromide in tetrahydrofuran followed by addition of aldehydes at 0 °C provided secondary alcohols **5a-5e** in excellent yields. Esterification of these alcohols with ethyl malonyl chloride and pyridine in tetrahydrofuran at 0 °C for 3 h afforded the malonates **6a-**

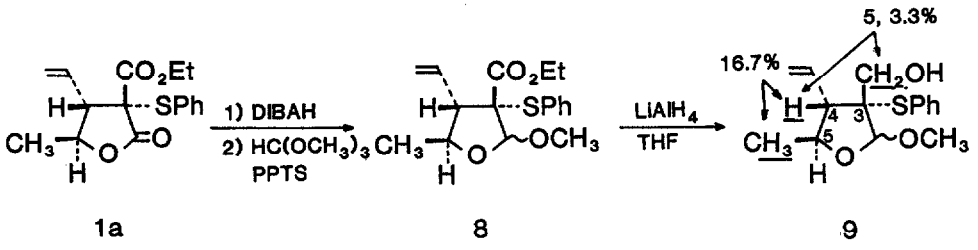


Scheme 1

6e in high yields.[5] Selective hydrogenation of the triple bonds in these malonates on 5% Pd-$BaSO_4$ provided the desired Z-olefins **7a-7e** without formation of the corresponding E-isomers. Reaction of **7a-7e** with p-toluenesulfonyl azide and triethylamine in acetonitrile at 45 °C for 40 h yielded diazo esters **2a-2e** in excellent yields.[5] While several attempts for the generation of carbenes from these diazo esters by employing a typical copper catalyst such as copper powder or cupric sulfate turned out the recovery of substrates or formation of intractable mixtures, treatment of the diazo esters **2a-2e** with a catalytic amount of rhodium acetate (0.01 equiv.),[6] freshly prepared from rhodium chloride,[7] in refluxing benzene, afforded γ-butyrolactones **1a-1e**[8] as single stereoisomers in moderate to good yields.

The stereochemistry of substituents on the lactone ring in **1a-1e** was assigned based on NOE experiments of compound **9**, which was derived from **1a** by diisobutylaluminum hydride reduction, acetalization of the resulting hemiacetal, followed by lithium aluminum hydride reduction (Scheme 2). A large NOE was observed between C(4)-H (δ 3.17) and C(5)-CH_3 (δ 1.33) and between C(4)-H and methylene protons (δ 3.74 and 3.87) of C(3)-CH_2OH in **9**. These results obviously demonstrate that an alkyl group (R) orients equa-

torially in the preferred transition state (3a).



1a 8 9

Scheme 2

The experimental procedure for the rearrangement is as follows; after a solution of **2** (1 mmol) and freshly prepared rhodium acetate[7] in benzene (6--8 mL) had been stirred for 10 min at room temperature, it was heated for 20 min at 80 °C. The resulting mixture was passed through a short silica gel column and removal of the solvent afforded crude **1**, which was purified by HPLC.

To our knowledge, the [2.3]sigmatropic rearrangement via eight-membered cyclic sulfonium ylide seems to be unprecedented. The products obtained here would be useful precursors for the corresponding 2,5-dihydro-5-alkyl-4-vinyl-2-furanone derivatives whose analogues have successfully been employed as building blocks in natural product synthesis.[9]

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8. (^{1}H NMR data at 90 MHz) **1a** 7.20-7.70 (m, 5H), 5.95 (ddd, 1H, J=18, 10.8, 8), 5.42 (dd, 1H, J=10.8, 1), 5.34 (dd, 1H, J=18, 1), 4.73 (dq, 1H, J=10, 6.5), 4.28 (q, 2H, J=6.5), 3.36 (dd, 1H, J=10, 8), 1.46 (d, 3H, J=6.5), 1.29 (t, 3H, J=6.5); **1b** 7.20-7.74 (m, 5H), 5.96 (ddd, 1H, J=17, 10.8, 8), 5.39 (d, 1H, J=10.8), 5.30 (dd, 1H, J=17, 2), 4.57 (ddd, 1H, J=10, 7.2, 3.6), 4.26 (q, 2H, J=6.5), 3.40 (dd, 1H, J=10.8, 8), 1.40-1.72 (m, 4H), 1.26 (t, 3H, J=6.5), 0.96 (t, 3H, J=5); **1c** 7.20-7.68 (m, 5H), 5.96 (ddd, 1H, J=18, 10.8, 8), 5.37 (d, 1H, J=10.8), 5.30 (dd, J=18, 2), 4.46 (dd, 1H, J=10, 5), 4.21 (q, 2H, J=6.5), 3.56 (dd, 1H, J=10, 8), 1.94 (m, 1H), 1.26 (t, 3H, J=6.5), 1.04, 1.01 (d, 3H, J=6 each); **1d** 7.20-7.72 (m, 5H), 5.96 (ddd, 1H, J=18, 10.8, 8), 5.39 (d, 1H, J=10.8), 5.30 (dd, J=10.8, 2), 4.56 (m, H), 4.24 (q, 2H, J=6.5), 3.40 (dd, 1H, J=10, 8), 1.24-1.76 (m, 8H), 1.25 (t, 3H, J=6.5), 0.90 (t, 3H, J=6.5); **1e** 7.20-7.68 (m, 10H), 5.97 (ddd, J=18, 10.8, 8), 5.46 (d, 1H, J=10.8), 5.30 (dd, 1H, J=18, 2), 4.82 (ddd, 1H, J=10, 7, 4), 4.20 (q, 2H, J=6.5), 3.46 (dd, 1H, J=10.8, 8), 3.02 (m, 2H), 1.20 (t, 3H, J=6.5).

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