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# New Entry to γ,δ-Unsaturated Seven-membered Lactones

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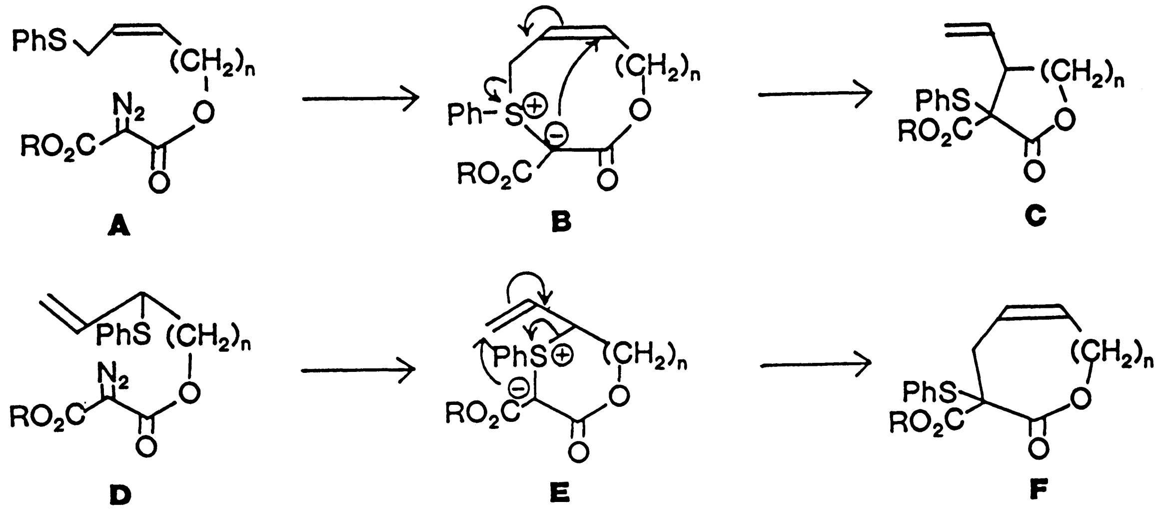
The [2,3]sigmatropic rearrangement of cyclic allylsulfonium ylides, generated from the diazo malonates of 2-phenylthio-3-butenol derivatives with catalytic rhodium acetate, afforded γ,δ-unsaturated seven-membered lactones in moderate to good yields.

We have recently developed the unexplored chemistry of cyclic allylsulfonium ylides and found a highly efficient synthetic method of functionalized five-[1)] (C: n=1) and six-membered lactones[2)] (C: n=2) by the [2,3]sigmatropic rearrangement of eight- and nine-membered cyclic allylsulfonium ylides (B) generated from acyclic diazo sulfides (A). To synthesize larger-sized lactones by applying this methodology, the sulfonium ylides intermediates are needed to take large cyclic structures, and high-dilution conditions would be required depending on the ring sizes of products. In addition, in our previous synthesis[1,2)] we needed Z-olefins as the substrates to fulfill stereochemical requirements of cyclic sulfonium ylide formation.

As an alternative approach to large-sized lactones, we envisioned that the reaction of diazo sulfide (D), isomeric to (A), would proceed through sulfonium ylide (E) having smaller cyclic structures than (B) to give lactone (F). In this paper we show this prognostication to be as expected.

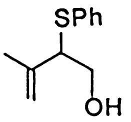
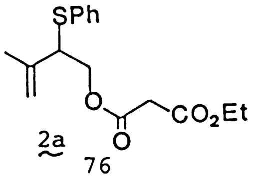
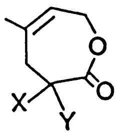
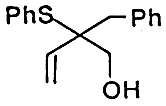
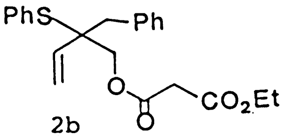
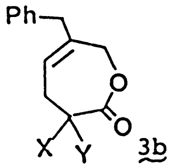
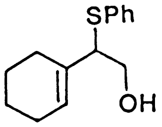
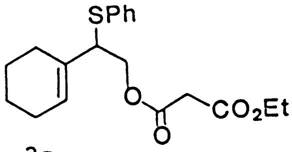
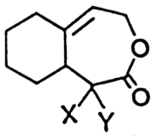
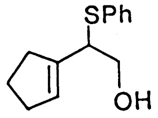
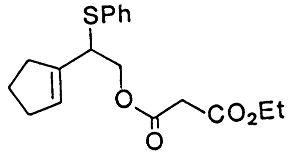
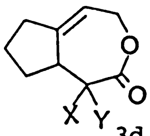
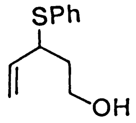
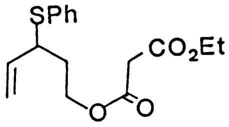
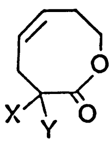


(n=1,2)

Substrate alcohols **1a** and **1b** were obtained from the known acetate[3] and ethyl 2-phenylthio-2-benzyl-3-butenoate[4] by hydrolysis and $LiAlH_4$ reduction, respectively (Table 1). Other alcohols **1c** and **1d** were prepared from 2-cyclohexylidene-[5] and 2-cyclopentylideneethanol[5] in 53 and 49% overall yields, respectively, by the known sequence of reactions,[3] i.e. 1) acetylation, 2) addition of phenylsulfenyl chloride, 3) dehydrochlorination, and 4) hydrolysis of the resulting unsaturated acetate with $K_2CO_3$ in methanol.[6] These alcohols were esterified with malonic acid monoethyl ester in dichloromethane at 30 °C by dicyclohexylcarbodiimide as condensing agent and 4-dimethylaminopyridine to give malonates **2a-d** in excellent yields. The malonates were submitted to the reaction with tosyl azide in acetonitrile containing triethylamine at 45 °C and the resulting crude diazo malonates were then treated with catalytic rhodium acetate (0.02 mol% of the substrate) in refluxing benzene to generate sulfonium ylides, giving $\gamma$, $\delta$-unsaturated seven-membered lactones **3a-d**[7] in moderate to good yields (entries 1-4).[8]

An attempt was made to extend this approach to the preparation of eight-membered lactones. In a similar manner, a diazo malonate obtained from homologous alcohol **1e**[9] through malonate **2e** afforded the expected

Table 1. Synthesis of γ,δ-Unsaturated Lactones

| Entry | Alcohol | Yield / % | |
|---|---|---|---|
| | | malonate | lactone[a,b] |
| 1 |  1a |  2a 76 |  3a 53 |
| 2 |  1b |  2b 95 |  3b 49 |
| 3 |  1c |  2c 88 |  3c 62 |
| 4 |  1d |  2d 89 |  3d 61 |
| 5 |  1e |  2e 90 |  3e 19 |

a) Yield based on the malonate 2. b) X, Y = PhS, $CO_2Et$.

unsaturated lactone (3e),[7] albeit only in low yield (entry 5).

References

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3) Y. Masaki, K. Hashimoto, and K. Kazi, Tetrahedron Lett., 19, 4539 (1978).

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6) All new compounds reported herein gave satisfactory spectral and microanalytical data.

7) ($^1$H NMR at 90 MHz) **3a**; 7.12-7.68 (m, 5H), 5.40 (br.s, 1H), 4.48 (m, 2H), 4.03 (q, 2H, J 7), 2.64 (br.s, 2H), 1.64 (s, 3H), 1.08 (t, 3H, J 7). **3b**; 7.00-7.64 (m, 10H), 5.56 (br.s, 1H), 4.60 (br.d, 1H, J 14.4), 4.28 (d, 1H, J 14.4), 4.10 (q, 2H, J 7.2), 3.32 (br.s, 2H), 2.84 (br.s, 2H), 1.14 (t, 3H, J 7.2). **3c**; 7.09-7.60 (m, 5H), 5.36 (dd, 1H, J 7.2, 3.5), 4.72 (dd, J 16.5, 3.5), 4.36 (dd, 1H, J 16.5, 7.2), 4.08 (q, 2H, J 7.2), 1.20 (t, 3H, J 7.2). **3d**; 7.20-7.72 (m, 5H), 5.64 (br.s, 1H), 5.12 (br.d, 1H, J 16.2), 4.68 (br.d, 1H, J 16.2), 4.12 (m, 2H), 3.60 (br.s, 1H), 1.16 (t, 3H, J 7.2). **3e**; 7.24-7.68 (m, 5H), 5.96 (m, 2H), 4.60 (dt, 1H, J 10.8, 2.8), 4.15 (q, 2H, J 7.2), 1.16 (t, 3H, J 7.2).

8) The lactones **3c** and **3d** were homogeneous from their $^1$NMR spectra though their stereostructures have not been assigned yet. Both ethoxycarbonyl and phenylsulfenyl groups are removable by reductive desufurization with zinc-acetic acid followed by deethoxycarbonylation of the resulting ester with NaCl in dimethyl sulfoxide (Ref. 2).

9) Obtained in 60% yield on the reaction of the lithium salt of allyl phenyl sulfide and ethylene oxide in THF at -78 °C.

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