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A NEW SYNTHESIS OF α,β-UNSATURATED γ- AND δ-LACTONES *VIA* INTRAMOLECULAR ACYLATION OF α-SULFINYL CARBANION

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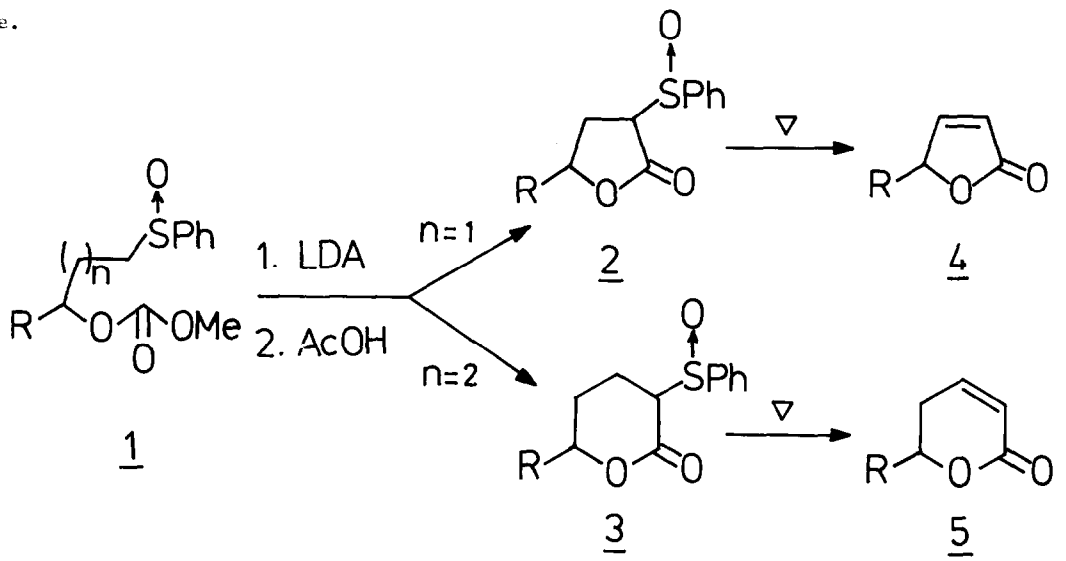
Summary: A new synthesis of α,β-unsaturated γ- and δ-lactones involving the intramolecular acylation of α-sulfinyl carbanion followed by pyrolysis is described.

α,β-Unsaturated γ- and δ-lactones are key structural subunits of natural products[1,2] and valuable synthetic intermediates.[2,3,7] As a consequence of their importance, many methods for the preparation of these compounds have been devised.[4] However, exploration of new procedures for construction of such frameworks from readily available acyclic precursors is still required. In connection with our studies on the intramolecular acylation of α-sulfinyl carbanions in organic synthesis,[5] we were interested in finding a new efficient and general method for preparation of α,β-unsaturated γ- and δ-lactones. Herein, we wish to describe a new synthesis of compounds 4 and 5 utilizing the intramolecular acylation of α-sulfinyl carbanion as shown in the following Scheme.



The cyclisation of the sulfoxide carbonate 1[6] to the α-phenylsulfinyl γ- and δ-lactones 2 and 3 was cleanly achieved by employing lithium diisopropylamide (LDA) in tetrahydrofuran (THF). Thus, treatment of 1 with LDA (2.0-2.2 equiv) in THF at -78° followed by warming to ambient temperature over 10 hr gave the cyclised products 2 and 3 in moderate to good yield after

quenching the mixture with glacial acetic acid followed by stirring at room temperature for 1 hr. Neat pyrolysis of the cyclised product 2 and 3 at 120°C under reduced pressure (0.05-0.1 torr) for 2 hr followed by preparative thin-layer chromatography (SiO_2) afforded the expected α,β-unsaturated γ- and δ-lactones in good yield. The results are summarized in Table 1. Compound 5b is massoia lactone, which is isolated from the bark oil of *Cryptocarya massoia*.[7,8]

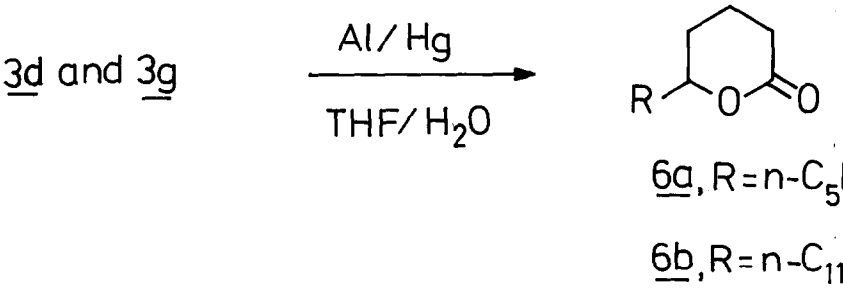
Table 1: Preparation of Compounds 2,3,4 and 5.

1	2 or 3 (%)[a,b]	4 or 5 (%)[a,b]
1: n = 1		
1a, R = H	2a (53)	4a (72)
1b, R = CH_3CH_2-	2b (79)	4b (68)
1c, R = *n*-$CH_3(CH_2)_3$-	2c (78)	4c (61)
1d, R = *n*-$CH_3(CH_2)_5$-	2d (80)	4d (76)
1e, R = *n*-$CH_3(CH_2)_6$-	2e (72)	4e (58)
1f, R = *n*-$CH_3(CH_2)_{10}$-	2f (75)	4f (80)
1: n = 2		
1h, R = H	3a (53)	5a (85)
1i, R = Ph	3b (68)	5b (96)
1j, R = *n*-$CH_3(CH_2)_3$-	3c (85)	5c (86)
1k, R = *n*-$CH_3(CH_2)_4$-	3d (55)	5d (80)
1l, R = *n*-$CH_3(CH_2)_5$-	3e (87)	5e (85)
1m, R = *n*-$CH_3(CH_2)_6$-	3f (79)	5f (80)
1n, R = *n*-$CH_3(CH_2)_{10}$-	3g (83)	5g (87)

a) All products have been characterised by spectral data.

b) Isolated yield after silica gel preparative thin-layer chromatography.

Furthermore, the cyclised products of types 2 and 3 appear to be important intermediates for the preparation of the saturated γ- and δ-lactones which are of much value as flavor substances and insect pheromones.[9] Thus, treatment of the sulfoxides 3d and 3g with Al/Hg[10] in aqueous THF furnished the δ-lactones 6a and 6b in good yield. The δ-lactones 6b has been proposed to be the pheromone responsible for the social behavior of the oriental hornet, *Vespa orientalis*.[11]



The above results clearly show that the present cyclisation is of general use for the preparation of α,β-unsaturated γ- and δ-lactones as well as the saturated ones.

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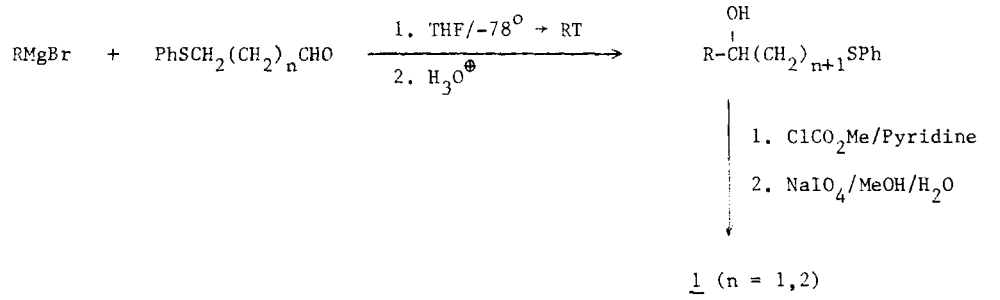
6. The sulfoxide carbonates 1 were prepared in good overall yields according to the following equation (cf. V. Reutrakul, P. Tuchinda and K. Kusamran, Chem.Lett., 1055 (1979).



1 (n = 1,2)

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