SULFUR DIOXIDE INSERTION INTO γ-FUNCTIONAL VINYLIC GRIGNARD REAGENTS. A FACILE SYNTHESIS OF α,β-UNSATURATED γ-SULTINES AND γ-SULTONES.

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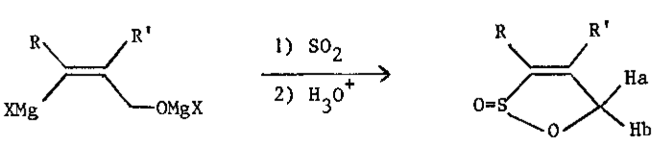
Abstract - α,β-Unsaturated γ-sultines were synthesised by insertion of sulfur dioxide into γ-functional vinylic Grignard reagents generated by addition of aliphatic or aromatic organomagnesium compounds to α-acetylenic alcohols. These products are easily oxidized to the corresponding γ-sultones.

We described recently the preparation of γ-functional vinylic Grignard reagents[1] and their reactions with halogenated[2] and carbonylated derivatives[3]. We particularly showed that $\Delta^{\alpha,\beta}$-butenolides can be easily obtained by addition of carbon dioxide to these compounds, and in this communication we report analogous reactions with sulfur dioxide.

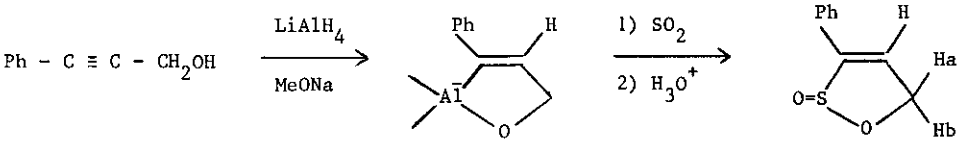
α,β-UNSATURATED γ-SULTINES

Although saturated γ-sultines can be easily prepared[4,5], only two methods are known for the preparation of the corresponding α,β-unsaturated compounds : pyrolysis of cyclic sulfones[6,7] or addition of bromine to allenic sulfinates[8]. We now report a new way of synthesising these compounds using vinylic Grignard reagents substituted by an hydroxyl group in the γ-position. Organomagnesium compounds are known to add to sulfur dioxide to give sulfinic acids after hydrolysis[9,10,11]. However vinylic sulfinic acids cannot be obtained by this route since polysulfones are rapidly formed[12]. In our case, the hydroxyl group in γ-position of the sulfinic acid allows, by intramolecular cyclisation, the formation of unsaturated esters of sulfinic acids or γ-sultines :



1 R = H, R' = Et
2 R = H, R' = Ph
3 R = H, R' = allyl
4 R = Ph, R' = Et
5 R = Ph, R' = Ph

Experimental and spectra data for these new compounds are given Table 1. Preparation of 1 is representatively described as follows. Ethylmagnesium bromide (125 ml, 2 M) in ether was added at -10°C with stirring to a solution of propargyl alcohol (5.6 g, 100 mmol) and copper iodide (1.9 g, 10 mmol) in anhydrous ether (100 ml). After stirring at room temperature for 15 h, the reaction mixture was added dropwise to a solution of the Et_3N-SO_2 complex[13], at -30°C (this complex gives sultines of a better purity than SO_2 alone), prepared by saturating anhydrous Et_3N (30.3 g, 300 mmol) with dry SO_2 followed by dilution with ether (50 ml). After stirring for 1 h at -30°C, the mixture was hydrolysed with saturated ammonium chloride solution (200 ml) followed by addition of NaOH (10%) until the aqueous layer was basic. After ether extraction, the aqueous layer was acidified to pH = 2 with HCl (5 M) and then reextracted with ether. The ethereal layer was washed with Na_2CO_3 (10%, 100 ml) and dried ($MgSO_4$). Evaporation of solvent at reduced pressure gave the crude compounds ; yields, mp's / bp's are given in Table 1. Sultines with R' = H were obtained in low yield using, instead of vinylic Grignard reagents, the vinylic aluminium compound 6[14] :



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α,β-UNSATURATED γ-SULTONES

Oxidation of sultines to sultones can be carried out with m-chloroperbenzoic acid but purification is difficult due to the presence of chlorobenzoic acid. A more convenient oxidising agent is potassium hydrogenopersulfate (oxone) (used by Trost[15] to oxidise sulfides to sulfoxides or sulfones). In this case unsaturated γ-sulfones are obtained in good yield (1→8, 2→9) (Table 2). The preparation of 8 is representatively described. A solution of 1 (1.4 g, 7.8 mmol) in MeOH (50 ml) was added to a suspension of oxone (8 g) in water (50 ml). After 4 h under reflux, filtration, ether extraction, drying, and concentration under reduced pressure gave 8 in a pure state.

A study of the reactivity of these compounds is in progress.

Table 1. Experimental and Spectral Data of α,β-Unsaturated γ-Sultines

Product N°	Yield (%)	Bp (°C/torr) mp(°C)	^{1}H NMR (a) (b) (solvent)
1	30	90 - 94/0.2	5.9 (1H, m, H vinylic) 4.95 (1H, m, Ha) 4.45 (1H, m, Hb) 1.85 (2H, q) 1.30 (3H,t) $J_{H\ vinylic-Ha}$ = 2.2 ; $J_{H\ vinylic-Hb}$ = 2 J_{Ha-Hb} = 15 (C_6D_6)
2	60	49	7.25 (5H, m) 6.75 (1H, m, H vinylic) 5.6 (1H, m, Ha) ; 5.2 (1H, m, Hb) $J_{H\ vinylic-Ha}$ = 2.4 $J_{H\ vinylic-Hb}$ = 2.4 (CCl_4)
3	32	100/1	6.45 (1H, m)6.3-4.8 (5H, m) 3.15 (2H, m) (C_3D_6O)
4	40	130/0.8	7.3 (5H, m) 5.54 (1H, m, Ha) 5.22 (1H, m, Hb) 2.35 (2H, q) 1.15 (3H, t) J_{Ha-Hb} = 15.3 (CCl_4)
5	24	84 (c)	7.2-7.3 (10H, m) 5.82 (1H, d, Ha) 5.55 (1H, d, Hb) J_{Ha-Hb} = 15 (CCl_4)
7	7	76 (d)	7.45 (5H, m) 7.05 (1H, m, H vinylic) 5.65 (1H, m, Ha) 5.35 (1H, m, Hb) $J_{H\ vinylic-Ha}$ = 1.9 $J_{H\ vinylic-Hb}$ = 2.2 J_{Ha-Hb} = 16 (C_3D_6O)

(a) δ in ppm from TMS, J values in Hz.

(b) From ref. (16) S=O and C-Ha bonds are syn.

(c) Recrystallized from toluene.

(d) Recrystallized from 40/60 petroleum-ether.

Table 2. Experimental and Spectral Data of α,β-Unsaturated γ-Sultones

Product N°	Yield (%)	mp (°C)	^{1}H NMR (a) (solvent)
8	60	48	6.55 (1H, m) 4.9 (2H, d) 2.4 (2H, q) 1.2 (3H, t) (C_3D_6O)
9	80	109	7.45 (5H, m) 7.3 (1H, t) 5.4 (2H, d) $J_{H\ vinylic-H\ allylic}$ = 1.5 (C_3D_6O)

(a) δ in ppm from TMS, J values in Hz.

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Received, 2nd July, 1982