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USE OF ALUMINA FOR ELIMINATION OF SULFINIC ACID FROM β-ARYL- AND β-ALKYLSULFONYL CARBONYL COMPOUNDS.

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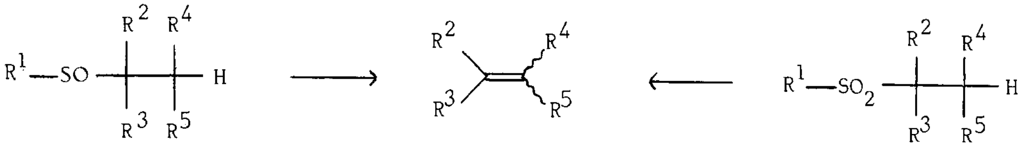
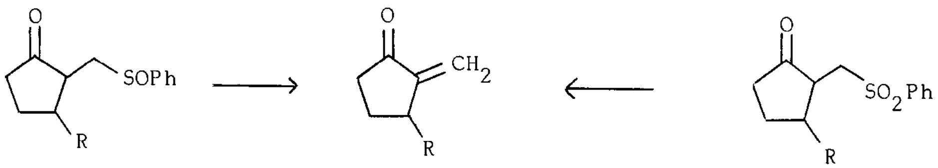
Abstract. Title compounds give α-unsaturated carbonyl compounds by treatment with basic alumina in dichloromethane or diethylether. α-Enones are thus obtained in high yield at room temperature.

Formation of unsaturated compounds from sulfoxides by thermal elimination of sulfenic acid[1,2] is well documented. Such an elimination has also been run in several cases in basic medium [1] or on silica gel at room temperature [3]. The same process from sulfones is also well known by elimination of sulfinic acid in basic medium [2,4].



We tried to apply these methods to prepare nitrile 3 and ester 4 corresponding to (d,l)sarkomycin from the corresponding sulfoxides 1, 2 or sulfones 5, 6 but we obtained unsatisfactory results.

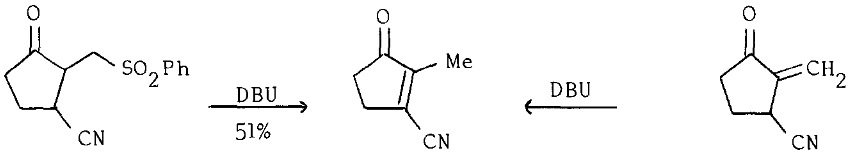


1 R = CN
2 R = COOMe

3 R = CN
4 R = COOMe

5 R = CN
6 R = COOMe

For instance heating [1,2] sulfoxides 1, 2 or silica gel treatment [3] of these compounds gave impure elimination products 3, 4 in low yield [5]. Sulfinic acid elimination from sulfone 5 in the presence of 1,8-diazabicyclo [5.4.O] 7-undecene (DBU) (1 equivalent) in CH_2Cl_2 at room temperature gave 7 as the only identified product which was isolated in 51% yield. This reaction probably proceeds via



5 7 3

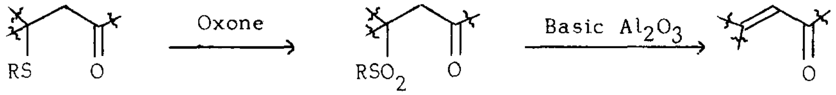
the formation of the expected product 3 followed by a fast isomerization into 7. We indeed noticed the total disappearance of 3 (^1H NMR, $CDCl_3$, δ 5.77, d, and 6.18, d, J = 3 Hz, two vinylic H) and the formation of 7 (^1H NMR, CCl_4, δ 1.85, t, J = 2 Hz, CH_3) within 15 min when 3 was treated by 0.15 equivalent of DBU in these conditions. Finally, we obtained satisfactory results by treatment of sulfones 5, 6 with basic alumina [5,6] ; a similar elimination was mentioned in a recent report[7]. The purpose of this communication is to extend this method to other cases and show its eventual limitations.

Several β-arylthio and β-alkylthio ketones and one β-arylthio aldehyde were oxidized to sulfones by oxone [8] and the crude compounds were treated with basic alumina ; the elimination products were obtained in satisfactory to high overall yield (see table). The same products were obtained in mild conditions by T. Nishio and Y. Omote [3] via oxidation to sulfoxides followed by silica gel treatment but in several cases in lower overall yield (58% for 8 ⟶ 14, 89% for 11 ⟶ 15, 92% for 12 ⟶ 16 and 69% for 17, but starting from 3-ethylthio 3-phenyl propionaldehyde).

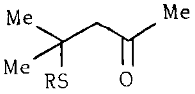
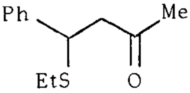
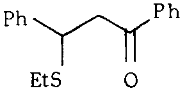
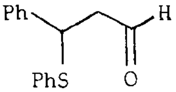
In our conditions, elimination were faster in diethylether than in dichloromethane (entries 1 and 2) ; however dichloromethane was used in most cases because of solubility problems.

Relative rates of sulfinic acid elimination were in the following order : $EtSO_2H < PhSO_2H < pNO_2C_6H_4SO_2H$ (entries 1, 3 and 4), however, in the last case the oxidation step was slow and the yield was moderate.

Table

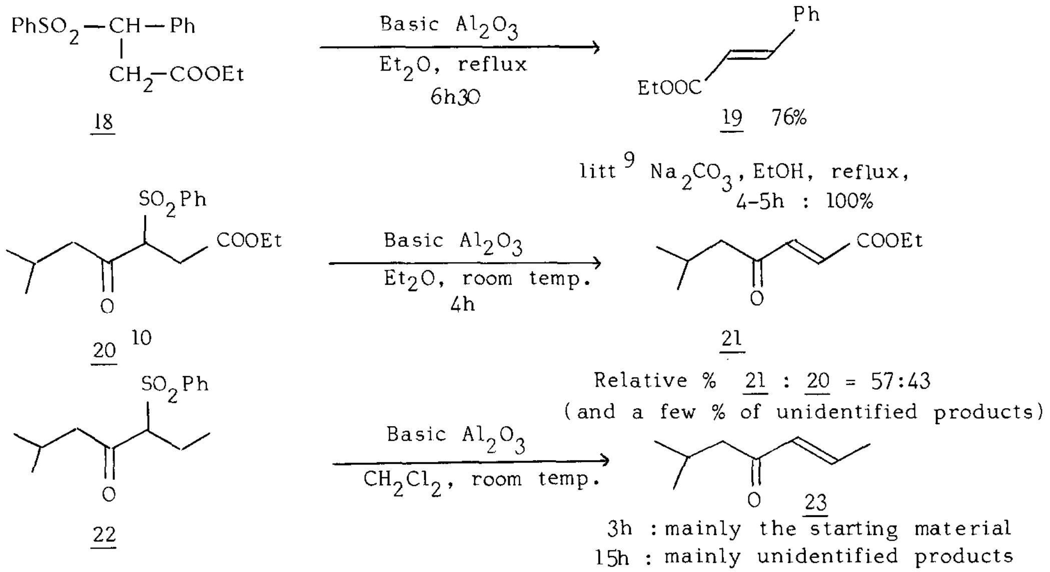


(only (E)-isomer)

Entry	Starting material		Oxidation time [a]	Elimination time	Yield [d]	Product
						
1	R = Et	8	6 h	225 min [b]	99	14
2	R = Et	8	6 h	180 min [c]	99	14
3	R = Ph	9	4 h	165 min [b]	91	14
4	R = $pNO_2C_6H_4$	10	25 h	120 min [b]	67[e]	14
5		11	6 h	40 min [b]	96	15
6		12	6 h	60 min [b]	97	16
7		13	2 h	12 min [b]	65	17

a) Room temperature except for 13 (1 h at 0°C and 1 h at room temperature) ; b) Room temperature, solvent CH_2Cl_2 ; c) Room temperature, solvent Et_2O ; d) Overall yield (2 steps) in pure product (however in the case of 14 a small amount of solvent remained after evaporation and was evaluated by NMR). Spectral data were identical with the ones of authentic samples ; e) Moderate yield due to the oxidation step.

When the hydrogen to be removed was less acidic, the reaction was much slower or even did not take place as seen from the three following examples.



This elimination of sulfinic acid from sulfones on basic alumina gives therefore very good results from sufficiently acidic compounds. The yields are high, the experimental conditions are very convenient and further unwanted reactions such as isomerization or polymerization may be avoided.

Experimental procedure 5 ⟶ 15

The oxidation of 5 (3 mmol) by oxone ($2KHSO_5$, $KHSO_4$, K_2SO_4)[8] gave the crude corresponding sulfone which was dissolved in CH_2Cl_2 (0.1 M solution). Basic alumina Fluka 5016A, activity I[11] (10.5 g) was then added to this solution in 5 min under stirring. After 40 min stirring (TLC monitoring) the solid phase (Al_2O_3 and sulfinic acid adsorbed on Al_2O_3) was separated by suction filtration on a sintered glass funnel. The solid was washed with CH_2Cl_2 (3 x 15 ml) and the solvent was evaporated leaving the pure product 15. (Yields of 16 and 17 (see Table) are given after purification by column chromatography on silica gel).

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10) The following compound : iPrCH2COCH2SO2Ph (prepared from iPrCH2COOEt and PhSO2Me in the presence of NaH, DMSO) was alkylated (in the presence of NaH, DMSO) either with BrCH2COOEt to give 20 or with EtBr to give 22.
11) Using alumina from a freshly opened new flask gives good results ; if necessary, it can be dried by heating several hours at 160°C under 0.1 torr.

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