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A NEW PROCEDURE FOR DESULFONYLATION: PREPARATION OF β-SUBSTITUTED α,β-UNSATURATED KETONES AND ALDEHYDES

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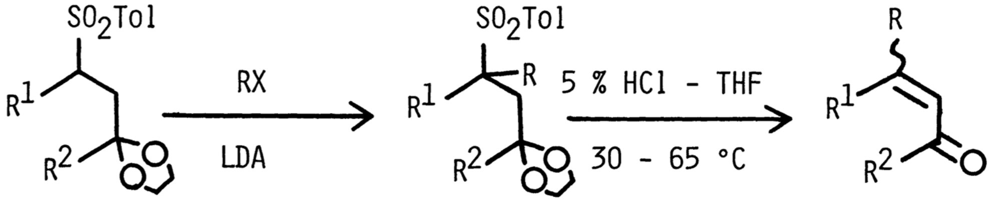
The treatment of the tert-alkyl sulfones bearing carbonyl group at the β-position with 5 % hydrochloric acid in THF at 30 - 65 °C afforded β-substituted α,β-unsaturated ketones and aldehydes in excellent yields.

In recent years, many organic sulfur compounds are used as key intermediates in the synthesis of natural products.$^{1)}$ We also reported the synthesis of the jasmonoids and 2,15-hexadecanedione using sulfones.$^{2)}$ The desulfonylation for making a variety of double bonds has been used in natural products synthesis as a potential procedure. For example, Julia et al. reported the synthesis of the carotenoids by treatment of the allylic sulfones with a strong base.$^{3)}$ The reductive elimination of sulfonyl group has been carried out by using aluminum amalgam, sodium amalgam, and zinc-acetic acid,$^{4)}$ and also a few examples of the base-induced desulfonylation to α,β-unsaturated carbonyl compounds have been reported.$^{5)}$

However, the acid-catalyzed desulfonylation of the *tert*-alkyl sulfones a has not been reported yet. We wish to report herein a new and general method of the desulfonylation. β-Substituted α,β-unsaturated ketones and aldehydes b were obtained in nearly quantitative yield by treatment of the sulfones a with 5 % hydrochloric acid in THF as shown in the following Scheme.



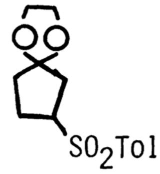
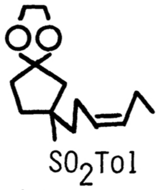
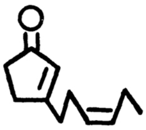
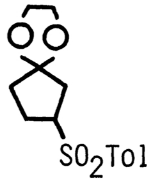
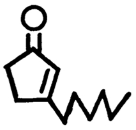
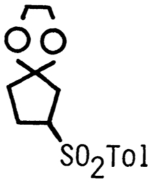
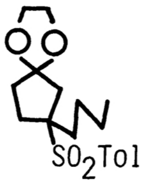
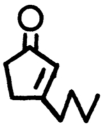
a b

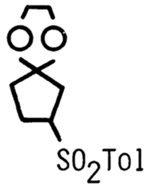
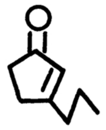
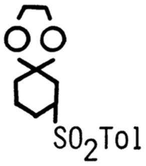
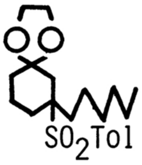
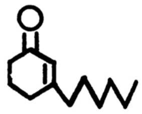
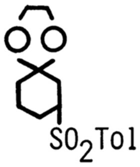
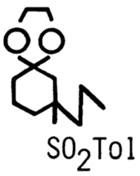
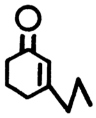
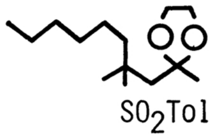
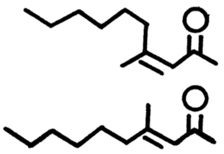
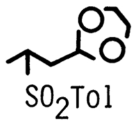
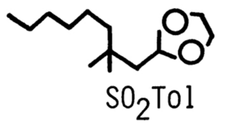
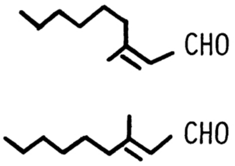
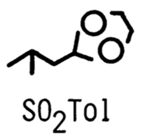
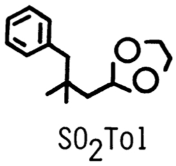
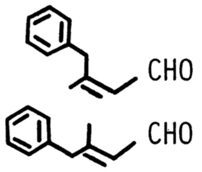
R	R^1	R^2
alkyl group	alkyl group	CH_3 or H
"	$-CH_2CH_2-$	
"	$-CH_2CH_2CH_2-$	

A typical experimental procedure is as follows. 1,1-Ethylenedioxy-3-(p-toluenesulfonyl)cyclopentane was alkylated using LDA and 1-bromohexane to give 1,1-ethylenedioxy-3-hexyl-3-(p-toluenesulfonyl)cyclopentane 2a as a viscous liquid in quantitative yield [IR(neat) 1600, 1320, 1270, 1120 cm^{-1}. NMR(CCl_4) δ 0.75 - 1.1 (3H, br), 1.15 - 1.95 (12H, br), 2.48 (3H, s), 2.1 - 2.9 (4H, m), 3.84 (4H, s), 7.34, 7.84 ppm (4H, an A_2B_2 pattern, J = 7.5 Hz)]. To a stirred solution of 2a (1 g, 28 mmol) in THF (20 ml) was added 5 % hydrochloric acid (6 ml). The stirring was continued for 4 h at 50 °C. The mixture was poured onto 300 ml of water. The organic layer was extracted with ether. The extract was washed with water, dried over anhydrous sodium sulfate, concentrated, and distilled (bp. 104 - 106 °C / 6 Torr) to give 3-hexyl-2-cyclopenten-1-one (0.41 g) in 90 % yield [IR(neat) 1720, 1620 cm^{-1}. NMR(CCl_4) δ 0.75 - 1.1 (3H, br), 1.1 - 1.9 (8H, br), 2.2 - 2.7 (6H, m), 5.93 ppm (1H, s)].

Table shows the results of the alkylation of the *sec*-alkyl sulfones and the desulfonylation of the *tert*- alkyl sulfones a. In run 1, 3-(*cis*-3-hexen-1-yl)-2-cyclopenten-1-one 1b was obtained from 1,1-ethylenedioxy-3-(*cis*-hexen-1-yl)-3-(p-toluenesulfonyl)cyclopentane 1a in 90 % yield.6) Similarly, The six-memberd ring sulfones, run 5 and 6, gave 3-alkylcyclohexenone derivatives in good yields, respectively. In run 7, a (E) and (Z) mixture of 4-methyl-3-decen-2-ones was obtained from 2,2-ethylenedioxy-4-methyl-4-(p-toluenesulfonyl)decane in 50 % yield. In run 8 and 9, aliphatic aldehydes, 3-methyl-2-nonen-1-one, 3-benzyl-2-buten-1-one, were prepared from the corresponding *tert*- alkyl sulfones in 90 % yields, respectively.

Table Preparation of β-Substituted α,β-Unsaturated Ketones and Aldehydes

Run	*sec* -Alkyl Sulfone	Alkylating Agent	*tert* -Alkyl[a] Sulfone	Products	Yield[b] (%)
1		1-bromo-*cis*-3-hexene			90
2		1-bromo-hexane			90
3		1-bromo-butane			90

4		1-bromo-propane				90
5		1-bromo-hexane				90
6		1-bromo-propane				90
7		1-bromo-hexane			4 : 6	50[c]
8		1-bromo-hexane			4 : 6	90[c]
9		α-chloro-toluene			4 : 6	90[c]

(a) The *tert*-alkyl sulfones were obtained in quantitative yield.

(b) Yield of isolated product.

(c) The ratios of (E) and (Z) were determined by GLC.

(d) All the compounds gave satisfactory NMR and IR spectra.

The reactions by use of sulfones and applications for the synthesis of natural products are under investigation.

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6) The details and applications for the synthesis of *cis*-jasmone from 3-(*cis*-3-hexen-1-yl)-2-cyclopenten-1-one are going to be published elsewhere.

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