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A FACILE METHOD FOR THE α-METHYLENATION OF SULFONES[1]

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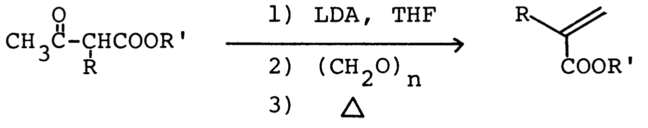
The carbanion of α-monosubstituted β-benzoylsulfones reacted with formaldehyde under mild conditions to afford α-methylenated products (α-alkylated vinylsulfones) in high yield with the elimination of a benzoate anion.

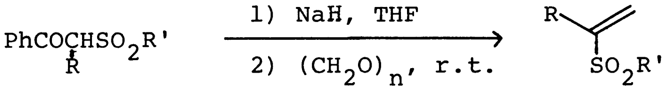
We have recently reported a new one pot method for the α-methylenation of esters or lactones by deacylative condensation, e.g., as shown in the equation [1].[2]



$CH_3\overset{O}{\overset{\|}{C}}-\underset{R}{\underset{|}{C}}HCOOR'$

.....[1]

To demonstrate the utility of this type of synthetically simple transformation, we have applied this methodology for the α-methylenation of sulfones. Vinylsulfones are known as useful synthetic intermediates for the C-C bond formation.[3] Thus, we found that the carbanions of α-alkylated β-benzoylsulfone (1) reacted with formaldehyde in tetrahydrofuran (THF) at room temperature for 5 hr to afford the desired methylenated sulfones (2) in 85-100% yield (eq., 2).



$PhCO\underset{R}{\underset{|}{C}}HSO_2R'$

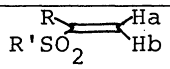
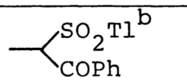
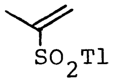
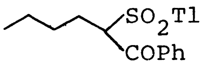
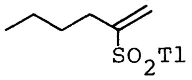
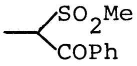
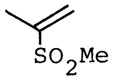
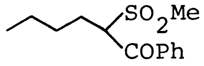
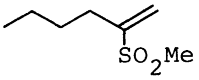
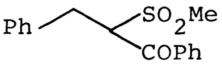
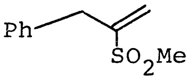
(1) (2)

.....[2]

The results are summarized in Table I. In every case studied here, no isomerization of the double bonds has been observed. It is also noteworthy that α-methylenation of sulfones (eq 2) proceeds efficiently at room temperature, whereas α-methylenation of esters (eq 1) at refluxing temperature of THF.

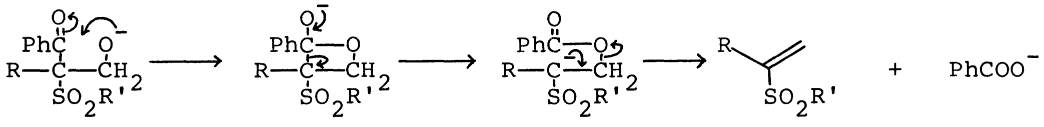
The general procedure is as follows; The reaction was carried out under nitrogen atmosphere. β-Benzoylsulfone (1) (2 mmol) in THF (5 ml) was added to a stirred suspension of sodium hydride (2 mmol) in THF (15 ml). After stirring at room temperature for 30 min, excess of solid paraformaldehyde (300 mg) was added and the resulting mixture was stirred for an additional 5 hr at room temperature. Excess paraformaldehyde and sodium benzoate were removed by filtration and the filtrate was concentrated to give the vinylsulfone (2), which was purified by chromatography (short active alumina column, eluted by chloroform). This procedure without employment of water at the work-up stage is essential to obtain the product sulfones (2) in high yield, since low molecular sulfones are often appreciably soluble in water.

Table I. Synthesis of Vinylsulfones (2)[4]

β-Benzoyl-sulfone (1)	Product (2)	Yield (%)	 (δppm)[a]		Bp [or mp] of (2)
		95	Ha; 5.65	Hb; 6.25	[52-55°C]
		99	5.67	6.17	139-140°C (1mm Hg)
		85	5.73	6.02	50-53°C (1mm Hg)
		100	5.76	6.19	73-75°C (1mm Hg)
		89	5.82	6.49	[31-32°C]

[a] In CCl_4. [b] Tl = p-tolyl

The reaction scheme may be best explained by the benzoyl transfer from carbon to oxygen atom followed by the elimination of a benzoate anion as follows.



(2)

In summary, the present methodology offers several advantages over the existing methods for the preparation of α-alkylated vinylsulfones[5] in the following aspects; 1) simple one pot reaction, 2) easiness of the separation of the product sulfones, and 3) introduction of the various kind of the substituents (R) is highly possible, since the substituent (R) (eq 2) is originally derived from alkyl halide (RX).[6]

References

1 Deacylative Condensation II. Part I, see Ref. 2.
2 Y. Ueno, H. Setoi, and M. Okawara, Tetrahedron Lett., 3753 (1978).
3 For example, see, P. D. Magnus, Tetrahedron, 33, 2019 (1977).
4 All compounds obtained here had satisfactory physical and spectral data.
5 For a similar independent work using gaseous formaldehyde which appeared after finishing-up of our manuscript, see H. Kotake, K. Inomata, and M. Sumita, Chem. Lett., 717 (1978).
6 The starting sulfones (1) were prepared by the alkylation of β-benzoylsulfones with appropriate alkyl harides (RX); H. O. House and J. K. Larson, J. Org. Chem., 33, 61 (1968).

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