(inner diameter 2.2 cm, inner volume 40 ml) were placed crotonic acid (4.30 g, 50 mmole) and urea (7.50 g, 125 mmole). The tube was sealed and was placed in an oil bath whose temperature was maintained at 195℃ for 2 h. After cooling to room temperature the mixture was taken out with aid of warm water (*ca.* 100 ml) and then heated to result a homogeneous solution. The water-insoluble polymeric gum was filtered off and the solution was decolarized with charcoal. Upon cooling slowly to room temperature white solid mass formed which was collected by filteration and dried under vacuum at 50℃ to give **2b**$_{eq}$ (1.17 g, 18%), mp. 217.5-218℃. The filtrate gave second crop after 3 days in a refrigerator, which was a mixture of **2b**$_{eq}$ and **2b**$_{ax}$ (1.44 g, 23%), mp. 186-187℃. Total yields of **2b**$_{eq}$ and **2b**$_{ax}$ were about 40% in several run.

Anal. **2e**: Calcd for $C_6H_{10}N_2O_2$: C, 50.69; H, 7.09; N, 19.70. Found: C, 50.88; H, 7.21; N, 20.03. **2f**: calcd for $C_7H_{12}N_2O_2$: C, 53.83, H, 7.74; N, 17.94. Found: C, 53.60; H, 7.68; N, 18.22. **2g**: Calcd for $C_7H_{12}N_2O_2$: C, 53.83; H, 7.74; N, 17.94. Found: C, 53.49; H, 7.55; N, 18.27.

An Illustrative Procedure for Preparation of 3: 5, 6-Dihydro-1,3-dimethyluracil (3a). A mixture of acrylic acid (3.6 g, 50 mmole) and 1,3-dimethylurea (3.60 g, 50 mmole) was placed in a stainless steel tube, sealed, and heated at 190℃ for 2 h. The liquid mixture was distilled under vacuum to give **3a** (4.65 g, 65%), bp. 88-92℃ at 0.08 mm.

Anal. **3a**: calcd for $C_6H_{10}N_2O_2$: C, 50.69; H, 7.09; N, 19.70. Found: C, 50.46; H, 7.27; N, 19.90. **3b**: calcd for $C_7H_{12}N_2O_2$: C, 53.83; H, 7.74; N, 17.94. Found: C, 53.62; H, 7.63; N, 17.87. **3c**: calcd for $C_7H_{12}N_2O_2$: C, 53.83; H, 7.74; N, 17.94. Found: C, 53.68; H, 7.86; N, 18.06. **3d**: calcd for $C_8H_{14}N_2O_2$: C, 56.45; H, 8.29; N, 16.46. Found: C, 56.66; H, 8.60; N, 16.38. **3e**: calcd for $C_8H_{14}N_2O_2$: C, 56.45; H, 8.29; N, 16.46. Found: C, 56.23; H, 8.57; N, 16.62. **3f**: calcd for $C_9H_{16}N_2O_2$: C, 58.67; H, 8.75; N, 15.20. Found: C, 58.38; H, 8.55; N, 15.50.

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Facile Synthesis of α-Allyl Substituted β-Oxo Sulfones

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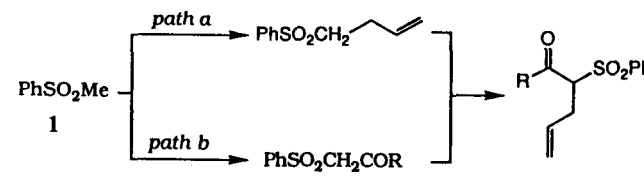
β-Keto sulfones are important building blocks and are widely used in synthetic organic chemistry.[1] The acidic nature of the methylene protons provides a convenient way of introducing various electrophiles at that position.[2] In the course of our studies on the reactivity of β-keto sulfones,[3] a consequence of our investigation of iodine-induced enoletherification of α-allyl substituted β-keto sulfones[4] was the requirement of an efficient method for synthesizing these compounds. We were surprised to find that no comprehensive method appear in the literature for the preparation of α-allyl substituted β-oxo sulfones.



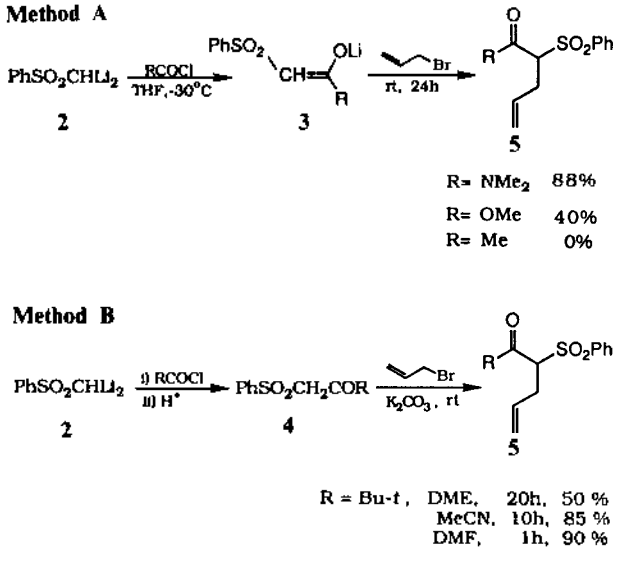
We first tried the allylation of methyl phenyl sulfone (**1**) and subsequent acylation (*path a*). However this reaction gave a problem to give di-allylated product.[5] Second, we assumed the acylation of methyl phenyl sulfone and subsequent allylation (*path b*). Fortunately β-keto sulfones were obtained in excellent yields from the reaction of acyl halides with 1,1-dilithiomethyl phenyl sulfone (**2**) which is easily generated by treatment of 2 equiv. of *n*-BuLi to a solution of methyl phenyl sulfone (**1**) in THF at −30℃.[6]

Therefore we tried *in situ* allylation of enolate (**3**) which is generated from reaction of acyl halide with 1,1-dilithiomethyl phenyl sulfone (**2**) (**Method A**). Only the reaction of allyl bromide with enolate **3** (R=NMe_2), which is generated *in situ* from N,N-dimethylcarbamyl chloride and sulfone di-

Table 1. Preparation of α-Allyl Substituted β-Oxo Sulfones (5) from Methyl Phenyl Sulfone

No.	R	Method	Condition	Yield (%)[a]	Mp. (℃)[b]
a	NMe_2	A	rt, 24 h	88	136-137
b	*t*-Bu	B	DME, rt, 20 h	50	91-92
		B	MeCN, rt, 10 h	85	
		B	DMF, rt, 1 h	90	
c	*c*-pr	B	DMF, rt, 1 h	83	38-39
d	*i*-pr	B	DMF, rt, 1 h	86	80-81
e	*n*-pr	B	MeCN, rt, 10 h	85	oil
f	Et	B	MeCN, rt, 10 h	88	oil
g	Me	B	DMF, rt, 1 h	86	oil
h	Ph	B	DMF, rt, 1 h	91	80.5-82
i	OMe	B	DMF, rt, 1 h	86	47.5-48.5
j	OPh	B	DMF, rt, 1 h	87	37-38

[a]Yield of isolated pure product. [b]Determined with a Fisher-Johns melting point apparatus and uncorrected.



anion (2) gave α-ally substituted β-oxoamido sulfone (5, R $=NMe_2$) in excellent yield. The reaction of allyl bromide with enolate (3, R=OMe) which is generated from methyl chloroformate and dianion (2) gave α-allyl substituted β-carbomethoxy sulfone (5, R=OMe) in moderate yield. However the reaction of allyl bromide with enolates generated from acyl halides did not give the allylated product.

Then we tried the allylation of the isolated β-keto sulfones (4) in polar solvent (**Method B**). In order to find out optimum conditions for the allylation of β-keto sulfones, we have examined several reaction conditions by using 4 (R=*t*-Bu) as a model compound. The reaction proceeded smoothly and cleanly in MeCN or DMF at room temperature in the presence of potassium carbonate. We also observed the solvent effect on the reaction. When DMF was used, the reaction progressed faster than that in MeCN or DME (entry b). As shown in Table 1, the present method was successfully applied to various β-oxo sulfones. The allylation of β-oxo sulfones in MeCN or DMF-potassium carbonate system gave only C-allylated product which is distinguished by ^{1}H-NMR and IR spectra.

Preparation of 5(R=NMe_2); Method A

A solution of methyl phenyl sulfone (3 mmol) in 10 m*l* of anhydrous THF was treated dropwise with a solution of 1.6 M *n*-BuLi (6.3 mmol) in hexane at −30℃. After 30 min of stirring at this temperature, the suspended reagent was treated dropwise with N,N-dimethylcarbamyl chloride (3.15 mmol) and stirred for 5 min. Then allyl bromide (4 mmol) was added to the reaction mixture. The resulting solution was warmed to room temperature and stirred for 24 h. Normal work-up gave a solid product which was recrystallized from carbon tetrachloride.

General Procedure; Method B

A solution of 1.6 M *n*-BuLi (6.3 mmol) in hexane was added slowly to a solution of methyl phenyl sulfone (3 mmol) in 10 m*l* of dry THF at −30℃. After 30 min, acyl chloride or chloroformate (3.5 mmol) was slowly added to the suspended reaction mixture. Subsequently, the reaction mixture was poured into 20 m*l* of saturated ammonium chloride solution and stirred. Normal work-up was performed. The crude β-keto sulfone was dissolved in 8 m*l* of DMF. Finely crushed potassium carbonate (3.2 mmol) and allyl bromide (3.2 mmol) were added and stirred for 1 h. The reaction mixture was poured into 10 m*l* of cold water. Normal work-up was performed. The desired product was isolated by flash column chromatography on silica gel using 1:3 EtOAc-hexane as an eluent.

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