

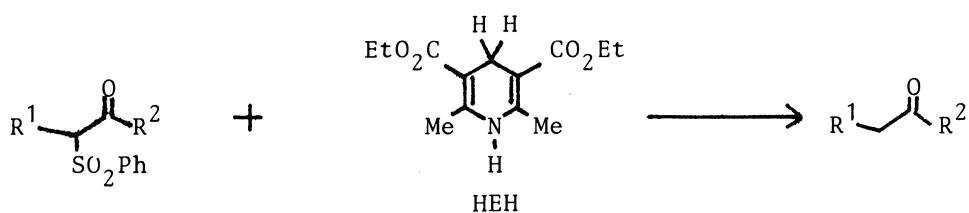
DESULFONYLATION OF  $\beta$ -KETO SULFONES WITH THE HANTZSCH ESTER, AN NAD(P)H MODEL<sup>1)</sup>

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Carbon-sulfur bonds in  $\beta$ -keto sulfones were reduced smoothly to carbon-hydrogen bonds with the Hantzsch ester, a model of NAD(P)H.

The replacement of C-S bonds in  $\beta$ -keto sulfones with C-H bonds is important in the synthesis of ketones because  $\beta$ -keto sulfones are easily alkylated and the reductive desulfonylation of the resulting alkylated  $\beta$ -keto sulfones gives alkylated ketones. A commonly used method for this purpose is the desulfonylation with aluminum amalgam.<sup>2)</sup> Although this method is useful in organic synthesis, amalgams are not favourable from the viewpoint of environmental pollution. We report here that Hantzsch ester (HEH), an NAD(P)H model, can convert a carbon-sulfur bond in a  $\beta$ -keto sulfone to a carbon-hydrogen bond<sup>3)</sup> in the presence of 0.01 equivalent of  $\text{RuCl}_2(\text{bpy})_3$  under irradiation of visible light.



The results are summarized in Table 1. Various  $\beta$ -keto sulfones were reduced to the corresponding ketones in good to excellent yields, whereas esters and olefins were inert under these conditions. Olefinic double bonds were not affected by the reduction. This reduction is specific for  $\beta$ -keto phenylsulfones; a methylsulfone and a *p*-nitrophenylsulfone were reduced only in low yields (<20%). Phenylsulfonyl groups adjacent to an ester or a nitrile group were not reduced. Thus, methyl 3-phenyl-2-(phenylsulfonyl)propionate and 3-phenyl-2-(phenylsulfonyl)propionitrile were not reduced.

In a typical experiment, a mixture of a  $\beta$ -keto sulfone (1 mmol), HEH (3 mmol) and  $\text{RuCl}_2(\text{bpy})_3$  (0.01 mmol) in 10 ml of pyridine were irradiated for 20 hours with a halogen lamp (Ushio halogen lamp JCD 100V-650WC) at room temperature under an argon atmosphere. The reaction mixture was poured into a 2 M hydrochloric acid and extracted with ether. The organic layer was washed with water and the product was extracted with ether. The ethereal solution was

washed with water and dried on sodium sulfate. After removal of the solvent *in vacuo*, the residue was chromatographed on silica gel with benzene as an eluent to obtain the corresponding ketone.

We believe that the present reduction has synthetic value as a new method for the desulfonylation of  $\beta$ -keto sulfones because the alkylation of  $\beta$ -keto sulfones is easy<sup>4)</sup> and resulting substituted ketones are useful compounds in organic syntheses. The application of this method to the synthesis of natural products is under investigation.

Table 1. Desulfonylation of  $\beta$ -keto sulfones with the Hantzsch ester

Substrate	Product	Yield/% <sup>a)</sup>	Substrate	Product	Yield/% <sup>a)</sup>
		74			81
		91			97
		83			14

a) Isolated yield.

#### References

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- 3) While the reductive desulfonylation of  $\alpha$ -nitrosulfones or allylic sulfones by NAD(P)H models have been reported,  $\beta$ -keto sulfones were inert under these conditions. Reduction of nitro sulfones with N-benzyl-1,4-dihydronicotinamide (BNAH)/DMF; N. Ono, R. Tamura, R. Tanikaga and A. Kaji, *J. Chem. Soc., Chem. Commun.*, 1981, 71; with BNAH/benzene/visible light; P.A. Wade, H.R. Hinney, N.V. Amin, P.D. Vail, S.D. Morrow, S.A. Hardinger, and M.S. Saft, *J. Org. Chem.*, 46, 765 (1981). Reduction of allylic sulfones with N-propyl-1,4-dihydronicotinamide/RhCl(PPh<sub>3</sub>)<sub>3</sub>/CH<sub>3</sub>CN; K. Nakamura, A. Ohno, and S. Oka, *Tetrahedron Lett.*, 24, 3335 (1983).
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