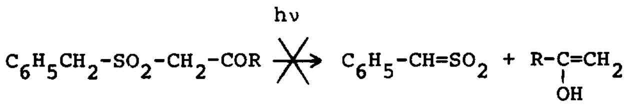
Tetrahedron Letters No.13, pp. 1165-1167, 1967. Pergamon Press Ltd. Printed in Great Britain.

PHOTOLYSIS OF α-DIAZO-β-KETOSULFONES AND β-KETOSULFONES[1]

A.M. van Leusen, P.M. Smid and J. Strating
Department of Organic Chemistry of the University,
Bloemsingel 10, Groningen, The Netherlands

(Received 23 January 1967)

A recent communication by De Mayo and co-workers[2] deals with unsuccessful attempts to obtain sulfenes by photolysis of benzylsulfonylmethyl ketones:



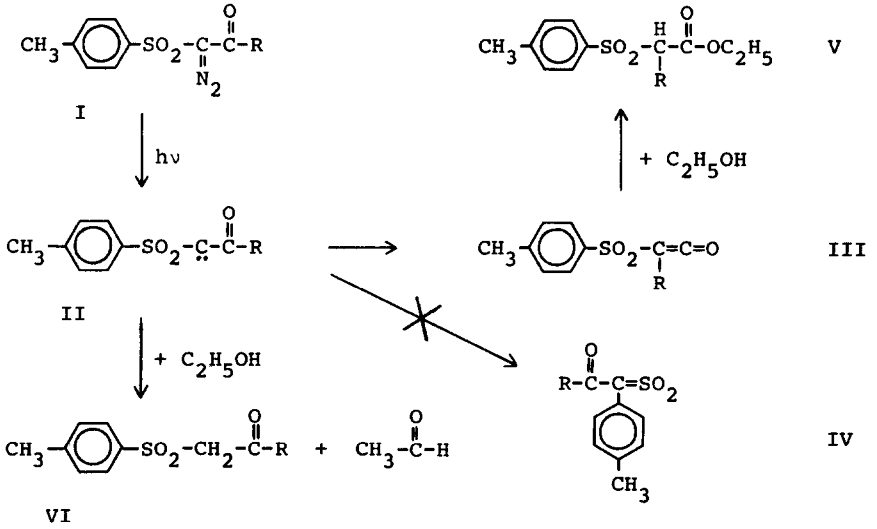
$$C_6H_5CH_2\text{-}SO_2\text{-}CH_2\text{-}COR \overset{h\nu}{\not\longrightarrow} C_6H_5\text{-}CH{=}SO_2 + R\text{-}\underset{OH}{C}{=}CH_2$$

No experimental evidence was found for such a Norrish Type II cleavage, involving transfer of a benzylic hydrogen to the carbonyl oxygen. Instead, all products appear to arise from simple cleavage of the carbon-sulfur bond beta to the carbonyl group. The main products are CH_3COR and benzylsulfinic acid.

Sulfenes, as well as photolysis of β-ketosulfones, are subjects of current work in this laboratory[3] also: this letter seems therefore justified.

A carbene II, generated by photolysis of I, might rearrange either to a ketene III (α-ketocarbene behaviour), or to a sulfene IV. From the reaction mixture obtained by irradiation[4] of α-acetyl-p-tolylsulfonyldiazomethane[5] (Ia) in ethanol was isolated ethyl α-(p-tolylsulfonyl)propionate (Va) (20%), the addition product of ethanol to IIIa. Furthermore 17% of acetonyl p-tolyl sulfone (VIa) (reduction product of IIa) and 45% of ethanal (as DNPH) were found. The addition product of ethanol to IV (ethyl α-acetyl-p-tolylmethanesulfonate) was not obtained. Again, the rearrangement of α-sulfonylcarbene to sulfene seems to be unfavourable[3].

Similarly, photolysis (45 min.) of α-benzoyl-p-tolylsulfonyldiazomethane[5] (Ib) provided benzoylmethyl p-tolyl sulfone (VIb) (33%), acetophenone (20% as DNPH) and more than one mole of ethanal (as DNPH). The presence of ethyl α-phenyl-p-tolylsulfonylacetate (Vb) (addition product of ethanol to IIIb) was indicated by TLC.



a) R = CH_3

b) R = C_6H_5

The formation of acetophenone and more than one mole of ethanal can be explained by subsequent photolytic decomposition of VIb to a benzoylmethyl free radical, which dehydrogenates additional ethanol. Shorter irradiation (30 min.) raises the yield of VIb to 85%.

It was established in separate experiments that indeed benzoylmethyl p-tolyl sulfone (VIb) gives acetophenone (68%) and ethanal (89%) upon irradiation (1 h) in ethanol. Our results, together with the recent reports in the literature[6], suggest exclusive cleavage of the sulfur-carbon bond in β-ketosulfones, and not between C=O and CH_2[7].

Considering the reasonable yields[6a], the photolytic ketone formation might have synthetic value, complementary to the reductive cleavage of β-ketosulfones (and β-ketosulfoxides) with aluminum amalgam[8]. In this respect, the efficient synthesis of β-ketosulfones from esters and dimethyl sulfone with tert-BuOK[9] or NaH[8] in DMSO is of interest.

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