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# SULFENES BY A 'WOLFF'-REARRANGEMENT OF SULFONYLCARBENES[1]

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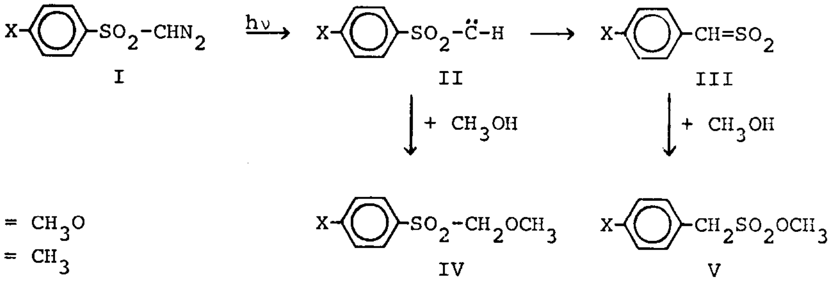
Three different types of reactions have been published, in which sulfenes ($R_2C=SO_2$) appear as transient species[2]. We now wish to report the first examples of sulfene-formation by rearrangement.

Evidence for the rearrangement of sulfonylcarbenes to sulfenes (II ⟶ III), as proposed in our previous papers[3,4] on sulfonylcarbenes, was obtained by the formation of benzylsulfonates V.



a) X = $CH_3O$
b) X = $CH_3$
c) X = H
d) X = $NO_2$

Irradiation of α-diazosulfone[5] Ia-d in methanol gives mainly aryl methoxymethyl sulfones, formed by insertion (II ⟶ IV). Part of the sulfonylcarbene[6], however, apparently rearranges to sulfene to form V, in a yield of about 10%.

## TABLE

Product composition from the irradiation of I

| $p\text{-}X\text{-}C_6H_4\text{-}SO_2CHN_2$ (I) | $p\text{-}X\text{-}C_6H_4\text{-}SO_2\text{-}CH_2OCH_3$ (IV) | $p\text{-}X\text{-}C_6H_4\text{-}CH_2SO_2OCH_3$ (V) |
|---|---|---|
| a) X = $CH_3O$ | 78%, m.p.[4] 56-57° | 12%, m.p. 60-61° |
| b) X = $CH_3$ | 76%, m.p.[7] 73-74° | 10%, m.p. 46-47° |
| c) X = H | 79%, m.p. 69-70° | 8%, m.p.[8] 60-61° |
| d) X = $NO_2$ | 32%, m.p. 98-100° | 7%, m.p.[8] 111-112° |

Diazosulfone I (500 mg in 50 ml of methanol) was irradiated with a Hanau S 81 high pressure mercury immersion lamp at -10° for 2 hrs under nitrogen, using a Pyrex filter. The compounds IVa-c and Va-c were isolated by prep. g.l.c., the yields were determined by anal. g.l.c., using internal standards. Compounds IVd and Vd, which decomposed in the gaschromatograph, were isolated by prep. thin layer chromatography. Therefore the yields of IVd and Vd must not be compared with those of IVa-c and Va-c. Satisfactory elemental analyses were obtained for all new compounds.

The tendency of the aryl group to migrate from sulfur to the carbene carbon is low, as is evident from the product composition (see Table). This is in contrast with the comparable rearrangement of ketocarbenes[9], $R\text{-}CO\text{-}\ddot{C}\text{-}H \longrightarrow R\text{-}CH{=}C{=}O$ (Wolff rearrangement). In the latter case, the main product is usually formed by rearrangement (i.e. the Arndt-Eistert synthesis of homologous carboxylic acid derivatives[9]). The sulfonyl group apparently lowers the migration aptitude of the aryl group.

An analogous difference is observed in nitrene[6] chemistry. Whereas acylnitrenes rearrange readily to isocyanates[10], $R\text{-}CO\text{-}\ddot{N}: \longrightarrow R\text{-}N{=}C{=}O$ (Curtius rearrangement), benzenesulfonylnitrene is found recently to undergo rearrangement to some extent only. Lwowski and Scheiffele[11] were able to isolate methyl phenylsulfamate in 23% yield from the reaction mixture obtained by irradiation of benzenesulfonyl azide in methanol ($C_6H_5SO_2\text{-}\ddot{N}: \longrightarrow C_6H_5N{=}SO_2 \xrightarrow{+\ CH_3OH} C_6H_5NH\text{-}SO_2OCH_3$).

Although the yields of Va-c (see Table) suggest a slight facilitation of the rearrangement II ⟶ III by electron-donating para substituents, the reproducibility of the yields has not yet been tested sufficiently to support this conclusion.

The products IVa-d* were found to be identical (by mixture m.p., IR and NMR spectra) with samples prepared by an independent route, as indicated:

$$RSH + ClCH_2OCH_3 \xrightarrow{C_2H_5ONa^{12}} RSCH_2OCH_3 \xrightarrow{[O]} RSO_2CH_2OCH_3 \quad (IV).$$

The oxidations were carried out with monoperphthalic acid; IVb was prepared previously[7] by oxidation with hydrogen peroxide in acetic acid.

Likewise compounds V were found to be identical (by retention times in g.l.c., IR and NMR spectra for Va-c, and by mixture m.p., IR and NMR spectra for Vd) with samples prepared[3] according to:

$$RCH_2Br + Na_2SO_3 \longrightarrow RCH_2SO_3Na \xrightarrow{(CH_3)_2SO_4,\ 100^{\circ}} RCH_2SO_2OCH_3 \quad (V).$$

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[*] During the preparation of this letter, two compounds, to which the structures of IVb and IVc were assigned, were reported by Schank[13]. Although the IR and NMR spectra are identical, the stability and melting points of his compounds differ clearly from ours. The properties assigned by Schank to α-alkoxysulfones must be incorrect, as will be discussed in the accompa^nying letter.

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