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THE ADDITION OF DIAZOMETHANE TO AROMATIC SULFINES

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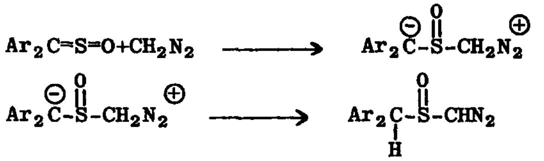
As part of a study of the reactions of sulfines with carbenoid reagents, we have initiated a study of the reactions of aromatic sulfines with diazo compounds. While this study was in progress, Strating and his coworkers reported that 9-diazofluorene reacts with dichlorosulfine to form 9-dichloromethylenefluorene.[2] We wish to communicate our results concerning the addition of diazomethane to aromatic sulfines.

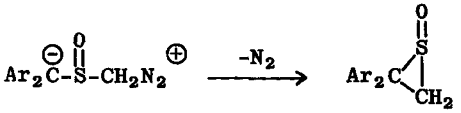
We considered that three possible reactions were likely. First, by analogy to the reaction of sulfines with enamines studied by Trippett[3] and by Sheppard and Diekmann,[4] addition of diazomethane might occur to give diazosulfoxides.



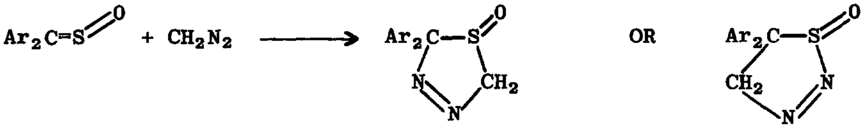
$$Ar_2C{=}S{=}O + CH_2N_2 \longrightarrow Ar_2\overset{\ominus}{C}-\overset{O}{\overset{\|}{S}}-CH_2\overset{\oplus}{N_2} \quad (I)$$

$$Ar_2\overset{\ominus}{C}-\overset{O}{\overset{\|}{S}}-CH_2\overset{\oplus}{N_2} \longrightarrow Ar_2\underset{H}{\underset{|}{C}}-\overset{O}{\overset{\|}{S}}-CHN_2$$

Second, by analogy to our own work on the reaction of 9-thiofluorenenone-S-oxide with trichloromethyl anion,[5] the intermediate I might undergo an internal displacement reaction reminiscent of the Ramberg-Backlund reaction[6] to give an episulfoxide.



Third, 1,3-dipolar addition of the diazomethane to the carbon-sulfur bond of the sulfine might occur to give Δ^3-1,3,4- or Δ^2-1,2,3-thiadiazoline-S-oxides.[2]



The sulfines were allowed to react with an excess of diazomethane in the dark under nitrogen at room temperature. Diphenylsulfine and di(p-anisyl) sulfine gave as the principal isolable products the corresponding 1,1-diaryl-ethylenes in 60% and 35% yields respectively. In the case of 9-thiofluorenone-S-oxide, the principal product is spiro[cyclopropane-1,9'-fluorene] which undoubtedly arises by further reaction of the initially formed dibenzofulvene with excess diazomethane.[7] Confirmation of the transitory presence of the fulvene is provided by the isolation of "polydibenzofulvene" from the reaction.[8] Whereas the diarylsulfines-diazomethane reactions evolve nitrogen for about 48 hours under the reaction conditions, the reaction of 9-thiofluorenone-S-oxide with diazomethane seems to be over in less than two hours. In an attempt to elucidate the structure of any intermediates, we treated 9-thiofluorenone-S-oxide with diazomethane in the dark at -25° C. After a few hours, the orange sulfine disappears and an unstable white solid is precipitated (m.p. 84° dec.).

We believe that this solid is a thiadiazoline-S-oxide on the basis of elemental analysis[‡] and on the following spectral data. A strong band in the infrared spectrum at 1550 cm.$^{-1}$ is assignable to the -N=N- stretch. Both pyrazolines[9] and 1,3,4-thiadiazolines[10,11] exhibit this band. A strong band at 1070 cm.$^{-1}$ is typical of a sulfoxide function. An AB quartet in the nmr spectrum (H_a, δ6.47 ppm; H_b, δ5.90 ppm; J_{AB} = 18.2 Hz) signals the presence

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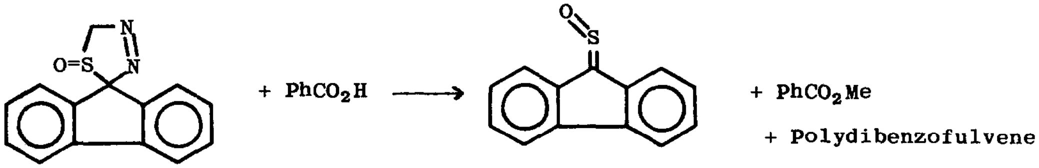
[‡] Although the compound is unstable, we were able to obtain an approximate analysis on freshly prepared solid, C = 67.2% H = 4.07% N = 10.1%. Calculated for $C_{14}H_{10}N_2OS$, C = 66.12% H = 3.90% N = 11.01%. We thank the Dallas Laboratories, Dallas, Texas, for special handling of the sample.

of dissymmetric sulfinyl function and the J_{gem} of 18.2 Hz is very close to the value of 17 Hz measured by Crawford and coworkers[9] in pyrazolines.

Without the proper model compounds, the nmr chemical shifts for the CH_2 protons of the thiadiazoline-S-oxide can not be used to distinguish between the two possible isomers, but we prefer the Δ^3-1,3,4-thiadiazoline-S-oxide structure simply on the basis that nucleophilic attack on diarylsulfines invariably occurs at sulfur, and so one would expect to find the more nucleophilic terminus of the diazomethane attached to sulfur.

When the thiadiazoline-S-oxide is allowed to decompose in an nmr tube and spectra are taken at intervals, the easily observable unique proton of thiofluorenone-S-oxide reappears at 8.7 ppm,[12] along with a singlet at 5.83 ppm which corresponds exactly to the chemical shift of the CH_2 protons of an authentic sample of dibenzofulvene.[8] Apparently, the thiadiazoline-S-oxide can both revert to starting materials and decompose to the observed products. To confirm the reversibility of the addition, the thiadiazoline-S-oxide was allowed to decompose in the presence of benzoic acid. Sixty-five mole per cent of the theoretically possible methyl benzoate was isolated, showing the presence of diazomethane. Polydibenzofulvene and starting sulfine are also isolable products of the decomposition.



Thus we postulate that diazomethane reacts with diaryl sulfines to form thiadiazoline-S-oxides, which then lose nitrogen to yield episulfoxides in the same manner that thiadiazolines yield episulfides.[10] The episulfoxides then lose sulfur monoxide to give the observed olefin products. In this connection, we wish to note that we have searched diligently for the relatively stable episulfoxide mentioned in footnote 16 of reference 2, but as yet have seen no evidence for its existence.

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