A Novel Preparation of Highly Substituted Sulphoxides from Sulphines

By A. G. SCHULTZ and R. H. SCHLESSINGER*

(*Department of Chemistry, University of Rochester, Rochester, New York* 14627)

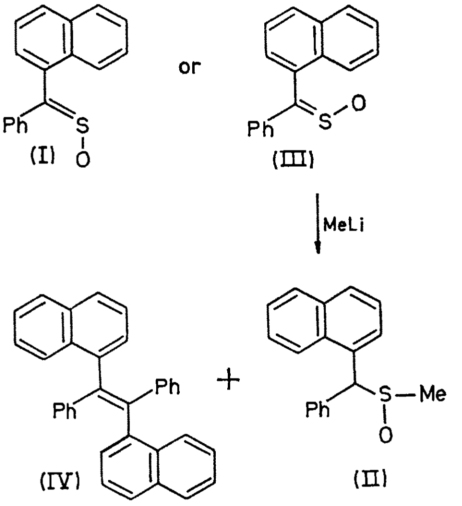
Summary Highly substituted sulphoxides are readily formed in an unusual reaction between sulphines and organolithium reagents.

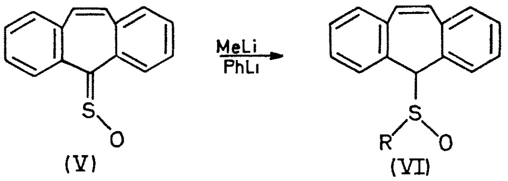
SIMPLE Hückel calculations carried out on $R_2C{=}S{\rightarrow}O$ type sulphines indicate that the sulphur atom in these unusual ylides is strongly electron-deficient.[1] These interesting theoretical results suggest that addition of carbon nucleophiles to sulphines should occur at sulphur to give sulphoxide anions. Surprisingly little is known about the reaction of sulphines with nucleophiles, however, and the apparent $C{=}S{\rightarrow}O$ polarization has not been utilized to synthetic advantage.[2] We have examined the behaviour of three readily available and differently substituted sulphines towards methyl- and phenyl-lithium in order to determine the effect of different $C{=}S{\rightarrow}O$ polarity on the reactions of sulphines and to develop a potentially useful synthesis of highly substituted sulphoxides.

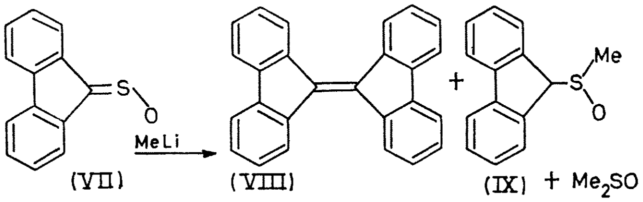
Reaction of the typically substituted diaryl sulphine (I)[3] in benzene solution (0·1 M) at 25° with 1 equiv. of methyl-lithium rapidly gave (2 min. reaction time) the methyl sulphoxide (II) (m.p. 131°) in 80% isolated yield.† Essentially the same results were obtained if an excess of methyl-lithium was used and longer reaction times employed. Sulphoxide (II) was also formed (80% yield) from sulphine (III),[3] the pyramidal isomer of (I). The n.m.r. spectrum of sulphoxide (II) showed sharp singlet resonance at δ 2·35 (CH_3·SO) and δ 5·44 (*C*H·SO) along with a complex multiplet of 12 aromatic protons between δ 6·80 and 8·00.‡ In addition to sulphoxide (II), a small amount (*ca.* 10%) of the dimeric hydrocarbon (IV) was obtained from either (I) or (III) under all reaction conditions.§

We have also studied the reaction of methyl-lithium with the sulphines derived from dibenztropone and fluorenone. Brief treatment (2 min.) of benzene solutions (0·1 M) of dibenztropone sulphine (V),¶ m.p. 101°, with 1 equiv. of methyl-lithium gave sulphoxide (VI; R = Me) m.p. 140° in nearly quantitative yield. The n.m.r. spectrum of (VI) showed singlet methyl proton resonance at δ 2·20, singlet methine proton resonance at δ 4·70, the vinyl protons as an AB quartet centred at δ 6·65 and 6·88 (J_{AB} 12 Hz), and a complex multiplet of aromatic protons between δ 7·00 and 7·50. No dimeric hydrocarbon could be detected in the reaction of sulphine (V) with methyl-lithium under the above conditions or using longer reaction times and an excess of lithium reagent.

In marked contrast, reaction of 1 equiv. of methyl-lithium with fluorenone sulphine (VII)[4] in 0·1 M-benzene solution for 2 min. gave a mixture consisting of difluorenylidene (VIII) (major reaction product), the methyl sulphoxide (IX), dimethyl sulphoxide, and sulphine (VII). On the other hand, treatment of a 0·01 M-solution of (VII) in benzene with 1 equiv. of methyl-lithium gave sulphoxide (IX) as the major product (45% yield based on unreacted starting material). The n.m.r. spectrum of (IX) showed a three-proton singlet (CH_3·SO) at δ 1·53, a one-proton singlet (*C*H·SO) at δ 5·25, and a complex multiplet of aromatic protons between δ 7·00 and 8·00.







Phenyl-lithium also reacts with sulphines (I) and (V) to give phenyl sulphoxides in good yield. For example, sulphine (V) treated with 1 equiv. of phenyl-lithium in benzene solution gives the corresponding phenyl sulphoxide (VI; R = Ph), m.p. 213° dec., in 70% yield.

The above results show that it is possible to add carbon nucleophiles to the sulphur atom of sulphines. It would appear that dimeric hydrocarbon formation is a significant side-reaction only when the initially-formed sulphoxide anion is unusually stabilized as in the case of the anion

---

† All m.ps are uncorrected. Satisfactory analyses were obtained for all new compounds.

‡ I.r. and mass spectral data consistent with the assigned structures were also obtained.

§ The presence of hydrocarbon (IV) was confirmed both by t.l.c. and g.l.c.–mass spec. analysis.

¶ Sulphine (V) was obtained in high overall yield from dibenztropone. The synthetic method used as the same as that employed for the preparation of sulphines (I) and (III), see ref. 3.

derived from fluorenone sulphine and methyl-lithium. More detailed comments on the mechanism of this dimerization reaction are given in the following communication.

The reaction of organolithium reagents with sulphines offers a potentially valuable synthetic route into otherwise difficultly accessible sulphoxides since new, direct, and high-yield syntheses of sulphines have recently been reported.[5]

We thank the Office of Naval Research at the University of Rochester for support of this work.

(*Received, May 1st*, 1970; *Com.* 646.)

---

[1] B. Zwanenburg, L. Thijs, and J. Strating, *Rec. Trav. chim.*, 1967, **86**, 577.

[2] The reaction of sulphines with triphenylphosphine has been reported by J. Strating, L. Thijs, and B. Zwanenburg, *Rec. Trav.chim.*, 1967, **86**, 641.

[3] R. H. Schlessinger and A. G. Schultz, *Tetrahedron Letters*, 1969, 4513.

[4] W. A. Sheppard and J. Diekman, *J. Amer. Chem. Soc.*, 1964, **86**, 1891.

[5] For a leading reference, see B. Zwanenburg, L. Thijs, and J. Strating, *Tetrahedron Letters*, 1968, 2871.