The Mechanism of Difluorenylidene Formation from Fluorenone Sulphine using Organolithium Bases

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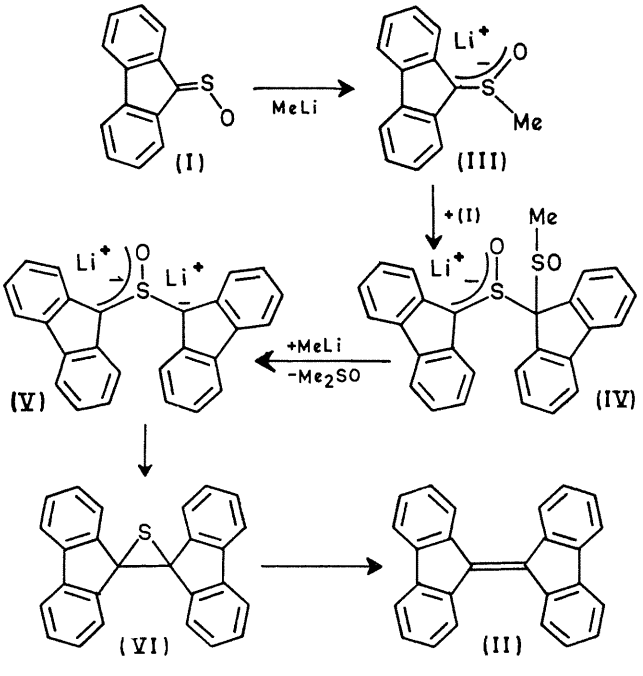
Summary Evidence is presented which suggests that the base-induced formation of difluorenylidene from fluorenone sulphine occurs through a sulphoxide dianion in a reaction sequence similar to the phenyl-lithium-promoted conversion of dibenzyl sulphoxide into stilbene.

IN the previous communication we described the reaction of three differently substituted sulphines with methyl- and phenyl-lithium.[1] All cases except fluorenone sulphine gave the corresponding methyl or phenyl sulphoxides in high yield. Surprisingly, fluorenone sulphine (I) underwent a ready dimerization reaction to yield the hydrocarbon difluorenylidene (II). The transformation (I)→(II) is similar to the phenyl-lithium-induced conversion of dibenzyl sulphoxide into stilbene.[2] Hence, a similar reaction mechanism (Scheme) was assumed for the formation of hydrocarbon (II) from sulphine (I). We now report some observations indicating that this is the correct mechanism for this novel reaction.



SCHEME

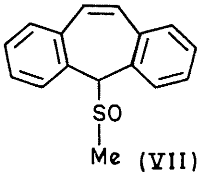
The Scheme is based on the assumption that initial reaction of sulphine (I) with methyl-lithium occurs to give the methyl sulphoxide anion (III) which in turn condenses with another molecule of sulphine (I) to give the disulphoxide monoanion (IV). Reaction of (IV) with another molecule of base would lead to the sulphoxide dianion (V). Dianions like (V) are known to collapse into episulphides,[2] and the conversion of episulphides such as (VI) into olefins is known to occur in the presence of a wide variety of bases, including methyl-lithium.[3]

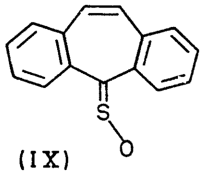
We have found that the formation of difluorenylidene from fluorenone sulphine depends not only on the concentration of sulphine but also on the number of equivalents of lithium base used in the reaction. For example, hydrocarbon (II) is the major reaction product when 0·1 M-benzene solutions of sulphine (I) are treated with 1 equiv. of methyl-lithium.[1] When 0·01 M-solutions of (I) are treated with 1 equiv. of methyl-lithium, the methyl sulphoxide (III) is the predominant product, accompanied by smaller amounts of the hydrocarbon.[1] Nearly complete conversion of (I) into difluorenylidene and dimethyl sulphoxide occurred when 2 equiv. of methyl-lithium was used. Both the concentration-dependence and base requirements observed are consistant with the Scheme.

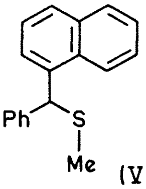
That the anion of sulphoxide (III) is involved in the formation of difluorenylidene from sulphine (I) is shown by the following experiments. Treatment of 0·1 M-benzene solutions of (III) with 1 equiv. of methyl-lithium gave rise to stable deep-red solutions. Addition of D_2O to these solutions after 3 min. and 5 min., followed by n.m.r. and mass-spectrometric analysis of the recovered sulphoxide (nearly quantitative) showed the methine carbon of (III; X = H or D) to be substituted with 50% and 90% deuterium, respectively. Reaction of (III) with 2 equiv. of methyl-lithium also gave stable deep-red solutions. When these solutions, after standing for 5 min., were treated with 1 equiv. of sulphine (I), the red colour was instantly discharged and the bright-orange hydrocarbon (II) and dimethyl sulphoxide were formed in good (70%) yield.

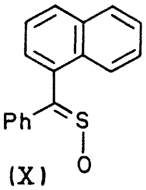
The conversion of (IV) into dianion (V) and the collapse of (V) ultimately leading to the hydrocarbon dimer are apparently fast reactions. When a deficiency of base was employed the only products which could be detected by n.m.r., mass spectrometry, and chromatographic analysis were hydrocarbon (II), sulphoxide (III), and unreacted sulphine (I). Decomposition of (IV) into (V) probably occurs by attack of the base (methyl-lithium) on the methyl-substituted sulphoxide sulphur atom, giving rise to dimethyl sulphoxide and dianion (V). This supposition is supported by the observation that phenyl-lithium also effects the high yield conversion of (I) into (II), accompanied by the formation of diphenyl sulphoxide.†

Sulphoxides (VII)[1] and (VIII),[1] when treated with methyl-lithium, do not give their corresponding anions, but rather undergo a very rapid sulphoxide cleavage reaction (as with IV) giving rise to the anions of 5*H*-dibenzo[*a*,*d*]cycloheptene and 1-benzylnaphthalene, respectively.† Stable anions of (VII) and (VIII) can be prepared by reaction of methyl-lithium with sulphines (IX) and (X).[1] These anions are deuteriated with D_2O exclusively at the methine carbon atom (>90% D incorporation) and are unreactive towards the sulphines from which they are derived.‡ Thus, the nucleophilic behaviour of the anion of sulphoxide (III) stands in marked contrast to that observed for the anions of sulphoxides (VII) and (VIII).


(VII)


(IX)


(VIII)


(X)

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† J. Jacobus and K. Mislow, *J. Amer. Chem. Soc.*, 1967, **89**, 5228, have postulated a different mechanism for this type of sulphoxide cleavage reaction involving, in the case of methyl sulphoxides, elimination of methylene sulphine ($CH_2{=}S{\rightarrow}O$). When the reaction (I)→(II) is carried out using phenyl-lithium, decomposition of intermediate (IV) (methyl replaced by phenyl) cannot proceed by the elimination reaction postulated by these authors. A brief experimental description of the reaction of methyl-lithium and fluorenone sulphine is also described by these authors. They obtained a complex mixture of products which by i.r. analysis contained fluorene and difluorenylidene. We have not detected fluorene in any of our reactions.

‡ As noted in ref. 1, the anion of (VIII) does react to a limited extent with sulphine (X) to give a dimeric hydrocarbon (10%).

[1] A. G. Schultz and R. H. Schlessinger, preceding communication.
[2] R. H. Schlessinger, G. S. Ponticello, A. G. Schultz, I. S. Ponticello, and J. M. Hoffman, jun., *Tetrahedron Letters*, 1968, 3963.
[3] R. D. Schuetz and R. L. Jacobs, *J. Org. Chem.*, 1961, **26**, 3467, and references cited therein.