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Reaction of Thiobenzophenone *S*-Oxide (Diphenylsulfine) with Carbon Nucleophiles

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Synopsis. The reaction of diphenylsulfine with a Grignard reagent or alkyllithium gives a variety of products depending on the structure of the Grignard reagent or alkyllithium.

2,2,4,4-Tetramethyl-3-pentanethione *S*-oxide (di-*t*-butylsulfine) reacts with Grignard reagents affording a variety of products depending on the structure of the Grignard reagent.[1] The reactions were interpreted in terms of a delicate competition of thiophilic attack (one-electron transfer process) and proton-abstraction (acid-base reaction).

In this paper we wish to describe the reactions of thiobenzophenone *S*-oxide (diphenylsulfine) with various carbanionic reagents. The results will be compared with those from the corresponding reactions of di-*t*-butylsulfine.

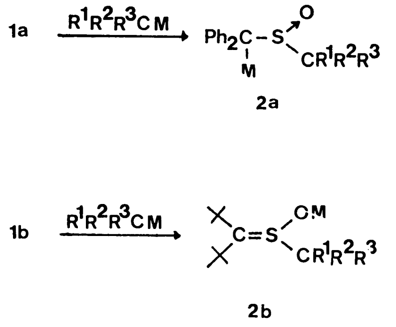
Results and Discussion

The reactions were carried out, in general, by adding a solution of diphenylsulfine, **1a**, to a solution containing

$R_2C{=}S{\rightarrow}O$
1a: R=Ph
1b: R=*t*-Bu

a three-fold excess of Grignard reagent at room temperature. However, it was confirmed that inverse addition did not change the products. Reaction conditions and products are summarized in Table 1 together with data from the reactions with alkyllithiums.

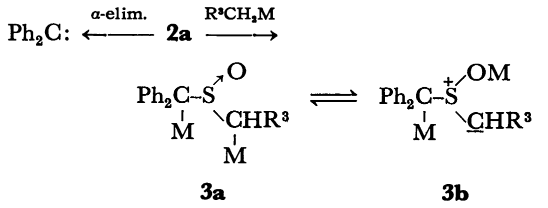
Products obtained by the present reactions are quite different in type from those obtained from the reactions of di-*t*-butylsulfine, **1b**. Detailed analyses of product distribution have revealed that the differences can be accounted for by the difference in the structure of initially formed anions.



(1)

The reaction course from **2a** seems to depend on the softness (polarizability, thiophilicity) and hardness (basicity) of the attacking reagent.

When a primary-alkyl reagent is employed in the reaction in DME, the hard base abstracts an acidic α-proton in **2a** resulting in the formation of a dianion, **3**, which is subsequently converted into an olefin through the corresponding thiocarbonyl ylide and thiirane. The electrocyclic ring-closure of a thiocarbonyl ylide has been reported.[2] Methyllithium in DME, on the other



(2)

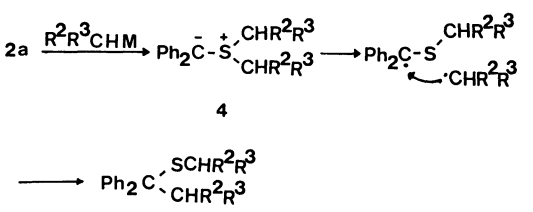
Table 1. Reaction of di phenylsulfine[a)]

Reagent	Solvent	Product (Yield/%)[b)]	Reagent	Solvent	Product (Yield/%)[b)]
CH_3MgI	Et_2O	$Ph_2C{=}CPh_2$ (77)	$PhCH_2MgCl$	Et_2O	$Ph_2\underset{\overset{\vert}{CH_2Ph}}{C}SCH_2Ph$ (86)
	DME	$Ph_2C{=}CH_2$ (69)		DME	$Ph_2C{=}CHPh$ (62)
CH_3Li	Et_2O	$PHCH\underset{\overset{\downarrow}{O}}{S}CH_3$ (87)	$Me_2CHMgCl$	Et_2O	$Ph_2\underset{\overset{\vert}{CHMe_2}}{C}SCHMe_2$ (69)
	DME	$Ph_2C{=}CH_2$ (64)		DME	$Ph_2CH\underset{\overset{\downarrow}{O}}{S}CHMe_2$ (78)
		Ph_2CHCH_3 (10)			
C_2H_5MgBr	Et_2O	$Ph_2C{=}CHCH_3$ (52)	$Et\underset{\overset{\vert}{Me}}{C}HMgCl$	Et_2O	$Ph_2\underset{\overset{\vert}{CH(Me)Et}}{C}SCH(Me)Et$ (78)
	DME	$Ph_2C{=}CHCH_3$ (41)	Me_3CMgCl	Et_2O	$Ph_2CH\underset{\overset{\downarrow}{O}}{S}CMe_3$ (32)
C_3H_7MgBr	Et_2O	$Ph_2C{=}CHEt$ (40)			$Ph_2C{=}CPh_2$ (6)
		$Ph_2\underset{\overset{\vert}{Pr}}{C}SPr$ (46)			Ph_2CH_2 (2)
C_3H_7Li[c)]	Et_2O	$Ph_2CH\underset{\overset{\downarrow}{O}}{S}Pr$ (92)			

a) At room temperature for 3 h. b) Isolated yield. c) At −20°C.

hand, is a very hard reagent, and the reaction with this reagent results in an α-elimination.[3-5] An extremely hard reagent, such as lithium compounds in ether, no further reaction takes place from **2a**. It is reported that both a sulfoxide and tetraarylethylene are formed by the reaction of a diarylsulfine with methyllithium in benzene.[6] Thus, the predominancy of a course (or courses) shown in Reaction 2 depends on the reaction conditions and reagents.

A secondary-alkyl reagent forms a sulfide by the reaction in ether. Since the secondary-carbanion is soft enough to attack the sulfur and a proton in **2a** is not acidic enough to be abstracted, the reaction scheme may be represented by Reaction 3. The process from **4**



(3)

to the sulfide is well-known as the Stevens rearrangement.[7,8]

Benzylmagnesium chloride undergoes the secondary alkyl-type reaction in ether, whereas it behaves as a primary-alkyl reagent in DME. This is a marked difference between the reactions of **1a** and **1b**.[1] A further difference between the reactions of **1a** and **1b** with a secondary-alkyl reagent is that **1a** affords a sulfide which is composed of two parts of the alkyl reagent, whereas the sulfide from **1b** has only one part.[1]

t-Butylmagnesium chloride is a very soft reagent and may behave similarly to the secondary-alkyl reagent. However, the product from this reagent was the sulfoxide. Probably the steric effect of two *t*-butyl and a diphenylmethyl groups prevents this reagent from attack on sulfur.

TABLE 2. REACTION OF DIPHENYLMETHYL ALKYL(OR ARYL) SULFOXIDE[a]

R in $Ph_2CH\text{-}\overset{\overset{O}{\uparrow}}{S}\text{-}R$	Reagent	Product	Yield/%[b]
CH_3	CH_3MgI	$Ph_2C{=}CH_2$	34
		Ph_2CH_2	28
CH_3	CH_3Li	$Ph_2C{=}CH_2$	13
		Ph_2CHCH_3	53
CH_3	$PhCH_2MgCl$	$Ph_2C{=}CH_2$	25
		Ph_2CH_2	31
Me_2CH	CH_3MgI	$Ph_2C{=}CH_2$	64
Me_2CH	CH_3Li	No reaction[c]	—
Me_2CH	C_4H_9Li	No reaction[c]	—
$PhCH_2$	CH_3Li	$Ph_2C{=}CHPh$	58
$PhCH_2$	C_4H_9Li	$Ph_2C{=}CHPh$	64
$PhCH_2$	$PhCH_2MgCl$	$Ph_2C{=}CHPh$	55
Ph	CH_3MgI	No reaction	—
Ph	C_4H_9Li	No reaction	—

a) At room temperature in 1,2-dimethoxyethane (DME). b) Isolated yield. c) The formation of carbanion was recognized by color and H-D exchange.

In the above discussion we proposed that **2a** is an universal intermediate in the present reactions. To test the intermediacy of **2a**, we studied the reactions from diphenylmethyl alkyl (or aryl) sulfoxide by abstracting an α-proton and the results are summarized in Table 2.[9] The formation of 1,1-diphenylethylene from diphenylmethyl methyl sulfoxide is consistent with the proposed reaction scheme. However, it is recognized, by the isolation of diphenylmethane, that S_N2-type displacement on sulfur takes place in DME competitively with the proton-abstraction.[10]

Experimental

Materials. Thiobenzophenone[11] and thiobenzophenone *S*-oxide[12] were prepared according to literature procedures. Ether and 1,2-dimethoxyethane were dried over sodium weire and distilled prior to use. Sulfoxides were obtained by oxidation of the corresponding sulfides.

General Procedure. All reactions were carried out under a nitrogen atmosphere with stirring. Into 6 mmol of a Grignard reagent (or an alkyllithium) in 10 ml of ether was added 1 mmol of the sulfine in 10 ml of ether (or 1,2-dimethoxyethane) or *vice versa*. No difference was recognized in the result by the change of the addition order. When equivalent amounts ef a Grignard reagent and the sulfine were reacted, the reaction became slower but the product was the same as that obtained from the above reaction, though the yield was poor. After usual work-up, the products were subjected to column chromatography over silica gel with hexane–benzene (4 : 1 v/v) eluent. Analytically pure products were obtained by means of preparative VPC on a Varian Aerograph 920. The same procedure was employed for the reaction of sulfoxides.

The structure of products were confirmed by the identity of spectral data with those authentic samples.

References

1) A. Ohno, M. Uohama, K. Nakamura, and S. Oka, *J. Org. Chem.*, **44**, 2244 (1979).

2) T. B. Cameron and H. W. Pinniek, *J. Am. Chem. Soc.*, **101**, 4755 (1979).

3) J. Hine and J. J. Porter, *J. Am. Chem. Soc.*, **82**, 6178 (1960).

4) E. Schaumann and W. Walter, *Chem. Ber.*, **107**, 3562 (1974).

5) A. Ohno, K. Nakamura, Y. Shizume, and S. Oka, *Bull. Chem. Soc. Jpn.*, **50**, 1003 (1977).

6) A. G. Schultz and R. H. Schlessinger, *J. Chem. Soc., Chem. Commun.*, **1970**, 746, 748.

7) W. Ando, *Acc. Chem. Res.*, **10**, 179 (1977).

8) E. Block, "Reactions of Organosulfur Compounds," Academic Press, New York, N. Y. (1978), pp. 118—119 and 198—201.

9) Because of the solubility of sulfoxides, the reaction could not be carried out in ether.

10) T. Durst, M. J. LeBelle, R. Van den Elen, and K.-C. Tin, *Can. J. Chem.*, **52**, 761 (1974).

11) R. Ahmed and W. Lwowski, *Tetrahedron Lett.*, **1969**, 3611.

12) B. Zwanenburg and L. Thijs, *Recl. Trav. Chim. Pays-Bas*, **86**, 577 (1967).