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COMPLEXES OF (METHYLSULFINYL)METHYLLITHIUM AND -SODIUM, WITH LEWIS BASES

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SUMMARY

A number of amine and ether complexes of (methylsulfinyl)methyllithium and sodium have been prepared and characterized. Complexes were only formed with the more strongly coordinating bases such as THF and dimethoxyethane; other bases, such as diethyl ether, did not complex, and uncomplexed $LiCH_2SOCH_3$ was isolated. The uncomplexed material, whether produced in a non-coordinating base or by desolvation of a complex, was extremely shock-sensitive, giving rapid spontaneous decomposition to sulfur-containing material. $LiCH_2SOCH_3$ reacted with acetylene to form an unstable complex of the formula $(LiC{\equiv}CH)_2 \cdot CH_3SOCH_3$.

INTRODUCTION

The synthesis and reactions of alkali metal (methylsulfinyl)methyls have been discussed in detail by Corey and Chaykovsky[1]. The major part of the work was carried out in dimethyl sulfoxide (DMSO) solution. Although Corey and Chaykovsky[1] reported that the reaction of n-butyllithium with DMSO in tetrahydrofuran solution resulted in precipitation of (methylsulfinyl)methyllithium (dimsyllithium)[2], it was not isolated or characterized.

Several amine and ether complexes of dimsyllithium and dimsylsodium have been prepared and characterized. Reaction of a slight excess of DMSO dissolved in the appropriate Lewis base with an organolithium compound resulted in precipitation of the complex of dimsyllithium in an exothermic reaction; the NaH reaction mixture had to be heated for several hours before the formation of dimsylsodium was complete. The solids were then isolated and their neutralization equivalents and per cents of lithium (from the total base) were determined. The compositions reported in Table 1 are based on these measurements. In order to confirm the neutralization equivalent results, an attempt was made to determine directly the DMSO/THF ratio of one complex by gas–liquid chromatography, using the technique of alcoholysis with 1,2,4-butanetriol in a pre-column. Unfortunately, decomposition to sulfur-containing products predominated over alcoholysis, and it was impossible to analyze the complex in this manner.

The dimethyl etherate of dimsyllithium was prepared by a somewhat different

TABLE 1

COMPOSITION OF $MCH_2SOCH_3 \cdot Z$ COMPLEXES

M	Z	Formula of complex	Neutralization equiv.		Decomp. temp.
			Calcd.	Found	
Li	$(CH_2)_4O$	$LiCH_2SOCH_3 \cdot (CH_2)_4O$	156	157	70°
	CH_3OCH_3	$LiCH_2SOCH_3 \cdot CH_3OCH_3$	130	131	71°
	$(C_2H_5)_2O$	$LiCH_2SOCH_3$	84	86	[a]
	$CH_3OCH_2CH_2OCH_3$	$(LiCH_2SOCH_3)_4 \cdot CH_3OCH_2CH_2OCH_3$	117	117	122°
	$(C_2H_5)_3N$	$LiCH_2SOCH_3$			[a]
	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	$LiCH_2SOCH_3$	84	83	70°
Na	$(CH_2)_4O$	$NaCH_2SOCH_3 \cdot (CH_2)_4O$	172	169	103°
	$CH_3OCH_2CH_2OCH_3$	$(NaCH_2SOCH_3)_4 \cdot CH_3OCH_2CH_2OCH_3$	122	120	127°

[a] Decomposed spontaneously.

procedure, the addition to DMSO of a benzene solution of dilithiodiisoprene dimethyl etherate[3].

Uncomplexed dimsyllithium was isolated by desolvation of $LiCH_2SOCH_3 \cdot CH_3OCH_3$ under vacuum at 40°. This compound was somewhat shock-sensitive, decomposing spontaneously and exothermically to a dark brown sulfur-containing material, although in an inert atmosphere. It was subsequently found that preparation of dimsyllithium in diethyl ether, triethylamine and tetramethylethylenediamine (TMEDA) also resulted in the formation of this uncomplexed product. It was possible to obtain a neutralization equivalent of the products prepared in diethyl ether and TMEDA, but several times the dimsyllithium decomposed in the inert-atmosphere dry box while samples were being taken. It appears that uncomplexed dimsyllithium is extremely shock-sensitive and should only be handled in small quantities. An attempted isolation of dimsylsodium by vacuum distillation of DMSO from a reaction mixture was also reported[4] to result in rapid decomposition or explosion.

A possible explanation for the decomposition is a reaction involving reduction of the sulfinyl group by a second molecule of dimsyllithium, similar to the reaction of DMSO with Grignard reagents[5].

$$2\,LiCH_2SOCH_3 \rightarrow LiOH + LiCH_2SOCH_2CH_2SCH_3 \xrightarrow{LiCH_2SOCH_3} \text{further reaction}$$

Another possible decomposition route would be that determined for the thermal decomposition of dimsyl ion in dimethyl sulfoxide by Price and Yukuta[6].

$$CH_3SOCH_2^- \rightarrow [CH_2] + CH_3SO^-$$

$$2\,CH_3SO^- \rightleftarrows CH_3S^- + CH_3SO_2^-$$

If the decomposition of solid dimsyllithium followed this route, however, some explanation for the fate of the methylene would have to be devised. Since no appreciable gas evolution took place, dimerization to ethylene did not take place, nor could reaction with dimsyl anion to form butadiene, as proposed by Price. Perhaps formation of polymethylene would be the major process in the solid state. It is also probable that, in the solid state, the decomposition is not an ionic process, and that neither of the two solution routes would be applicable.

Reaction of dimsyllithium·THF with benzophenone gave the expected hydroxysulfoxide in 91% yield with an infrared spectrum identical to that reported by Corey and Chaykovsky[1].

$$CH_3SOCH_2Li \cdot THF + Ph_2C{=}O \rightarrow Ph_2C(OH){-}CH_2SOCH_3$$

The THF complex reacted with acetylene in THF or hydrocarbon solution or in the solid state to give a lithium acetylide DMSO complex. The formation of this complex has also been reported by Kříž *et al.*[7]. The yellow solid complex was washed free of excess DMSO and analyzed by neutralization equivalent, giving a formula of $(LiC{\equiv}CH)_2 \cdot CH_3SOCH_3$ for the complex, which decomposed to $LiC{\equiv}CLi$ and acetylene, having a half-life of approximately four days in the solid state and in THF solution, and only several hours in a benzene suspension.

EXPERIMENTAL

Reagents

Dimethylsulfoxide (Crown-Zellerbach Corp.) was distilled under reduced pressure from calcium hydride and stored over calcium hydride. n-Butyllithium concentrate and dilithiodiisoprene dimethyl etherate in benzene (Lithium Corporation of America) and sodium hydride dispersions (Ventron Corp.) were commercial products used as received.

Analyses

Microanalyses were performed by Schwartzkopf Microanalytical Laboratories, Woodside, New York.

Procedure

The following procedures are illustrative of the methods used in the preparation and derivatization of the alkali metal (methylsulfinyl)methyls, and all of the reactions discussed in this paper may be performed by these procedures.

(Methylsulfinyl)methyllithium dimethyl etherate

To 65 ml of ether in a nitrogen-purged 250 ml 3-necked flask provided with an external cooling bath (dry ice/acetone) was added 3.9 g (0.05 mole) of dimethyl sulfoxide, previously distilled from calcium hydride. Dilithiodiisoprene dimethyl etherate (50 ml of a 1.0 *N* solution in benzene) was added dropwise to the reaction mixture kept at 0–10°. A white precipitate of the product began forming at once. When the addition was complete, the reaction mixture was transferred to a fritted glass filter funnel and pressure-filtered. The solid product was washed once with pentane and dried in a stream of argon to give 5.3 g (81.5%) of $CH_3SOCH_2Li \cdot CH_3OCH_3$ (decomposed on heating in an inert atmosphere at 71°). (Found: C, 36.37; H, 8.61; N.E., 131. $C_4H_{11}O_2S$ calcd.: C, 36.92; H, 8.46%; N.E., 130.)

(Methylsulfinyl)methyllithium tetrahydrofuranate

Dimethyl sulfoxide (7.8 g, 0.10 mole) was dissolved in 100 ml of THF in a nitrogen-purged flask equipped with dry-ice/acetone bath. Concentrated n-butyllithium[8] (8.9 ml of 95% n-butyllithium, 0.10 mole) was added dropwise at a rate sufficient to keep the reaction temperature between 0° and 10°. A white precipitate began to form almost at once. When the addition was complete, the reaction mixture was transferred to a fritted glass filter funnel and pressure-filtered. The solid product was washed once with pentane and dried in a stream of argon to give 12.9 g (83%) of $CH_3SOCH_2Li \cdot C_4H_8O$ (d. 70°). (Found: Li by total base, 4.51; N.E., 157. $C_6H_{13}LiO_2S$ calcd.: Li, 4.54%; N.E., 156.)

A 7.8 g (0.05 mole) sample of dimsyllithium · THF complex was reacted with 9.1 g (0.05 mole) of benzophenone in 100 ml of THF, to yield after hydrolysis and ether extraction, 11.8 g (91%) of 2-(methylsulfinyl)-1,1-diphenylethanol, m.p. 147–148° (lit.[1] m.p. 148–149°).

(Found: C, 69.61; H, 6.07; O, 12.5. $C_{15}H_{16}O_2S$ calcd.: C, 69.23; H, 7.15; O, 12.31%.) The infrared spectrum showed absorptions at 2.93 (OH), 3.31 (CH), 6.20, 6.63, 6.97, 14.90 (mono-substituted benzene), and at 8.17 (vs), (S=O), 9.40 (C–S), 9.80 (sulfoxide) μ.

(Methylsulfinyl)methylsodium tetrahydrofuranate

Dimethyl sulfoxide (21 g, 0.27 moles) was dissolved in 50 ml of THF in a nitrogen-purged flask, and sodium hydride (0.20 mole) as a 50% dispersion in mineral oil, was added all at once. Slow hydrogen evolution began almost at once; the reaction mixture was refluxed for $2\frac{1}{2}$ h at 65°, then cooled to 45° and stirred overnight. A gray precipitate formed, which was collected by filtration and dried in a stream of dry nitrogen, giving 26.1 g (76%) of $CH_3SOCH_2Na \cdot C_4H_8O$, d. 120–134°. (Found: active Na*, 13.4; N.E., 169. $C_6H_{13}O_2S$ calcd.: Na, 13.4%; N.E., 172.)

Lithium acetylide dimethyl sulfoxide complex

A sample of $LiCH_2SOCH_3 \cdot CH_3OCH_3$ (approx. 10 g) was suspended in a 1/1 pentane/benzene mixture and acetylene was introduced by means of a tube extending below the surface of the reaction. A yellow color developed in the solid. The suspension was filtered quickly through a fritted glass plate and dried with an argon stream to give $(LiC{\equiv}CH)_2 \cdot CH_3SOCH_3$. (Found: N.E., 69.72. C_2Li_2 calcd.: N.E., 19. C_4H_7LiOS calcd.: N.E., 103. $C_6H_8Li_2OS$ calcd.: N.E. 71.) The N.E. dropped to 23 over a five-day period of standing.

Derivatization with diisopropyl ketone

A 0.10 mole sample of $(LiC{\equiv}CH)_2 \cdot CH_3SOCH_3$ prepared in the above manner was dissolved in 75 ml of THF and neat diisopropyl ketone (14.0 g, 0.10 mole) was added over a 10-min period. The reaction mixture was hydrolyzed over a mixture of ice and acetic acid and extracted with ether. The extract was washed with $NaHCO_3$ and dried. An argentometric titration[9] indicated a yield of 94% of ethynyl diisopropyl carbinol. The product was identified by comparison with an authentic sample (prepared by reaction of the ketone with $LiC{\equiv}CH$ in liquid ammonia) on a Aerograph model 900 gas chromatograph, using a column consisting of 20% Carbowax 1000 on Chromosorb P at 128°.

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* Method[1]: Dimsylsodium (0.3265 g) was dissolved in 20 ml DMSO, 1.0 g of triphenylmethane was added, and the red solution was titrated to a yellow endpoint with 5.49 ml of 0.499 *N* sec-butanol in toluene.

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