

1,3-DIALKALI SALTS OF DIMETHYL SULFOXIDE\*

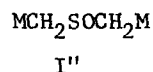
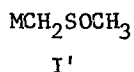
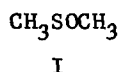
Edwin M. Kaiser and Robert D. Beard\*\*

Department of Chemistry, University of Missouri

Columbia, Missouri, 65201, U.S.A.

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Monoalkali salts (I') of dimethyl sulfoxide (DMSO) (I) have been routinely prepared in DMSO and other solvents by many basic reagents, some of which include sodium hydride (1), sodium amide (2), lithium amide (2), and n-butyllithium (2). However, the corresponding 1,3-dialkali salts (I'') of DMSO are unknown.



In this communication, we wish to report that 1,3-dialkali salts of DMSO may be rapidly and conveniently prepared by adding an ethereal solution of the sulfoxide to two molecular equivalents of an alkali amide (M = Li, Na, or K) in anhydrous liquid ammonia. Alternatively, addition of two equivalents of n-butyllithium to a solution of DMSO in tetrahydrofuran (THF)-hexane appears to similarly afford I'' (M = Li), though the latter reaction also leads to a variety of side-products.

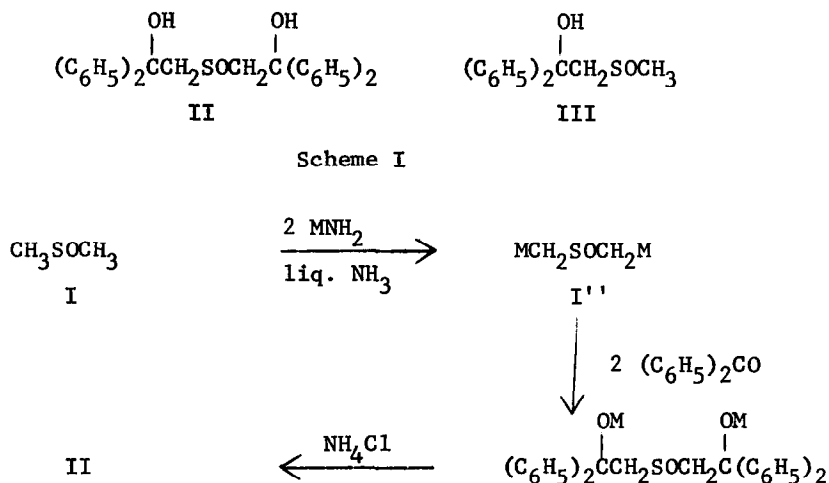
That dianion I'' (M = Li, Na, or K) was formed in liquid ammonia by

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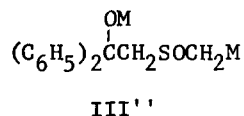
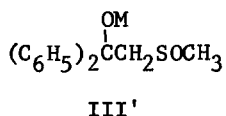
\*\* NDEA Fellow, 1966-present

the action of the appropriate alkali amide on DMSO was demonstrated by the addition of two equivalents of benzophenone to the reaction mixtures. Upon inverse neutralization, di- $\beta$ -hydroxysulfoxide II was obtained in 32% yield when M was lithium, in 42% yield when M was sodium, and in 15% yield when M was potassium (Scheme I). Small amounts of the known- $\beta$ -hydroxy-sulfoxide III (1) were also produced in these condensations.



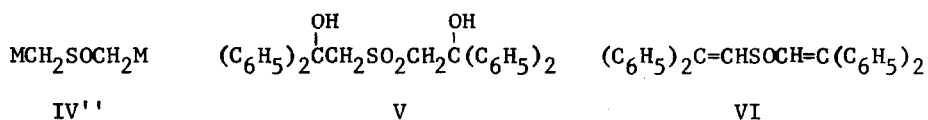
It was possible that diol II could have arisen in ammonia from step-wise ionization and condensation of DMSO with benzophenone. Thus, mono-anion I', formed first, could have undergone rapid condensation with the ketone to afford III' followed by ionization of the other methyl group to give III''; condensation of III'' would afford diol II (after hydrolysis). This possibility was tested and excluded by the following experiment. Mono-alcohol III was added to an equivalent of sodium amide in ammonia to presumably give alkoxide ion III'. After adding an equivalent of benzophenone (no apparent reaction), the reaction mixture was treated with an equivalent of sodium amide in ammonia. Now, the amide ion could have either ionized III' to give III'', or it could have added irreversibly to the ketone to afford  $(\text{C}_6\text{H}_5)_2\text{C}(\text{NH}_2)\text{ONa}$ , a compound which is stable in ammonia

but which decomposes to benzophenone and ammonia upon hydrolysis (3). The latter course occurred exclusively, though, since III and benzophenone were both recovered quantitatively; diol II was absent.



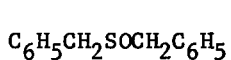
Incidentally, pure monoalcohol III may be easily prepared in liquid ammonia from monoalkali salt I' (M = Na). For example, addition of an ethereal solution of two equivalents of DMSO to 1.1 equivalents of sodium amide in ammonia followed by the addition of an equivalent of benzophenone afforded III in 69% yield. The use of an excess of DMSO was necessary to avoid contamination of III by diol II.

The results described above are analogous to those recently reported wherein the 1,3-dialkali salts (IV'') of dimethyl sulfone (IV) underwent two-fold aldol-type condensations with benzophenone in ammonia to afford di-β-hydroxysulfone V (4). Such two-fold condensations of I'' and IV'' are the only known examples in multiple anion chemistry where both anionic sites of a dicarbanion react with carbonyl compounds. Normally, only one such site enters into such condensation reactions (4).

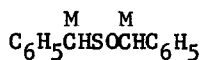


That diol II had the structure indicated was shown by satisfactory elemental analysis, and by infrared and n.m.r. spectroscopy. Surprisingly, analytically pure II melted at 157.5-159°, only 9.5-10.5° higher than the reported melting range of the mono-alcohol III (1). Diol II was also converted to the known diol V (4) by 30% hydrogen peroxide, and to divinyl-sulfoxide VI by 85% phosphoric acid.

The novel formation of the 1,3-dialkali salts of DMSO is rather remarkable in light of the known potassium t-butoxide catalyzed conversion of dibenzyl sulfoxide (VII) to stilbene in solvent dimethylformamide (5). It has not yet been established whether ethylene might be a by-product in our base-catalyzed reactions in liquid ammonia. However, similar treatment of dibenzyl sulfoxide with two equivalents of potassium amide in liquid ammonia to presumably form the corresponding dianion VII'' (6) followed by neutralization with ammonium chloride afforded only recovered sulfoxide; stilbene could not be detected in the reaction mixture.



VII



VII''

We are currently investigating the generality of the preparation and reactions of the 1,3-dialkali salts of other sulfoxides related to DMSO.

#### References:

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