

DMSO

The Dimethyl Sulfoxide (DMSO) Anion – Dimsyl Ion

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Introduction

One of the most useful strong bases in Dimethyl Sulfoxide (DMSO) is its anion, methyl sulfinyl carbanion, also called the dimsyl ion, first reported by Corey and Chaykovsky.¹ Dimsyl sodium solutions are easily prepared by stirring a mixture of sodium hydride or sodium amide in DMSO.² Because of its reactivity, the dimsyl ion is of great value in many organic synthesis reactions such as alkylations, nucleophilic displacements and condensations. The dimsyl ion is employed in analytical chemistry to quantitatively determine weak acids.

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Gaylord Chemical Company, L.L.C. (GCC) is the world's leading provider of Dimethyl Sulfoxide (DMSO) solutions. Beginning in the early 1960's, GCC has been dedicated to the development of new uses for DMSO. In order to meet customer-specific needs, GCC has pioneered the development of multiple grades of DMSO, including DMSO USP.

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Gaylord Chemical's headquarters are located in Slidell, Louisiana with manufacturing, research, and development facilities in nearby Bogalusa, Louisiana. GCC remains the only producer of DMSO in the Western Hemisphere.

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This bulletin describes some typical reactions and uses of this versatile reagent, its preparation, stability at various temperatures, and its decomposition reactions. It is recommended that chemists doing work with the dimsyl ion read the sections of the bulletin dealing with stability, general handling and safety considerations. Gaylord has performed syntheses of the dimsyl ion at scales up to 22 liters. Related information is included in the Dimsyl Ion Module and at our website, www.gaylordchem.com.

USES OF THE DIMSYL SODIUM REAGENT SOLUTION

The dimsyl sodium is a very versatile reagent that can be used in a wide number of organic and analytical applications. The dimsyl sodium solutions are easy to prepare, they are low in cost and solutions up to 3M can be prepared in the powerful solvent DMSO. As the base, the dimsyl sodium solution can be employed to remove protons from carbohydrates, amines, amides, acetylenes, weakly acidic hydrocarbons and many other compounds. The dimsyl ion has also been used to prepare salts of carbonyl compounds, and for eliminations producing olefins, aromatics and cyclopropane derivatives. There are numerous applications of the dimsyl ion in the isomerization of alkynes and formation of phosphorus ylides in preparing Wittig reagents. As a reactive anion, it adds readily to olefins and ketones to form beta-alkyl sulfoxides and beta-hydroxy sulfoxides while with esters it forms beta-keto sulfoxides. The dimsyl ion behaves like a typical carbanion in some nucleophilic displacements of benzyl or alkyl halides to give more complex sulfoxides. These and other applications of the dimsyl ion are described below.

As a Proton Removal Agent

By far the greatest number of applications of dimsyl sodium solutions involves its use as a base to remove protons from other molecules. Since the pKa of DMSO is 32-33,³ a variety of molecules more acidic than this can be readily converted to their anions. It has the advantage that when the dimsyl ion is protonated, a molecule molecule of DMSO. The possibility of side reactions are thus diminished because no other active species, such as water or alcohols are produced.

Carbohydrates and other polyhydroxy-materials that are soluble in DMSO may be easily converted to their sodium salts and methylated in the following step.^{4,5,6,7} Similarly, the sodium salts of polypeptides can be reacted by methylation⁸ or by graft polymerization at the anionic centers.⁹ Acetylenes are also converted to the sodium salts with the dimsyl ion. The alkylation of the acetylides is then performed in the DMSO suspension.¹⁰ In most cases, with the very weak carbon acids such as acetylenes, the intermediate sodium salts are rapidly consumed in the alkylation step so that the dimsyl sodium acts merely to initiate the sequence.

Materials more acidic than DMSO can be determined quantitatively by titration with the dimsyl ion using diphenylmethane or triphenylmethane as indicators. Aliphatic alcohols, phenols, acetic acid, morpholine, aniline, p-toluidine, hydrazine, dimethyl sulfone and many other weak "acids" have been determined this way.^{11,12,13} Hydrocarbons less acidic than triphenylmethane, such as cyclopentadiene, indene, fluorene, are also converted to their anions by dimsyl sodium and these can be used in subsequent reactions such as carbonation.^{14,11} These proton exchanges are very rapid reactions, and are catalyzed by trace amounts of alcohol.^{15,16,17}

Dimsyl ion solutions may be used to remove protons alpha to carbonyls to obtain anions which may react in the usual fashion, such as with esters^{18,19} or dienes.²⁰ The basicity of the dimsyl ion solutions may be used to obtain eliminations in a variety of situations to prepare olefins,^{20,22,1,19,23} to

obtain aromatic systems^{24,25,26,27} or to produce gamma elimination yielding cyclopropane derivatives.^{21,28,29} Similarly, the reagent has proven useful to isomerize 1-alkynes to conjugated dienes.³⁰

The dimsly sodium-DMSO reagent has frequently been used in the preparation of ylides. The phosphonium salts are converted to phosphonium ylides thereby providing a simple and convenient modification of the Wittig reaction.^{1,31,32,33,34,35,36,37} The conversion of sulfonium or oxosulfonium compounds into ylides, which then may be reacted in the same solution, is quite common.^{38,39,40,33}

The strongly basic dimsly sodium solution induces rearrangements such as the Wolff-Kischner reaction⁴¹ or that of trimethyl benzyl ammonium ions.⁴²

As a Nucleophile

The DMSO anion behaves as a typical carbanion by reacting with many alkylating agents to prepare more complex sulfoxides. Thus benzyl chloride⁴³, or other alkyl chlorides⁴⁴ and tosyl esters^{45,46,47,48} readily alkylate the DMSO anion. The dimsly anion reacts with epoxides by opening the ring to give beta-hydroxy sulfoxides.^{49,50,51} This reaction can initiate the polymerization of the epoxide leading to a chain containing the sulfoxide group.^{52,53}

Additions to Unsaturated Compounds

As a carbanion, the dimsly ion adds to some unsaturated systems. The interesting beta-keto sulfoxides containing a readily alkylated active methylene group⁵⁴ are prepared in high yield by addition to esters.^{44,55,56,57} The beta-keto sulfoxides undergo a Pummerer rearrangement by warming with acids producing oxidation at the alpha carbon such as in ninhydrin synthesis^{58,59,60}, and related reactions.^{61,62} Dimsly sodium also adds to an amide such as N,N-dimethyl formamide to yield an adduct which hydrolyzes to give methylsulfinylacetaldehyde.⁶³

Additions to other carbonyl compounds occur readily in high yields if the compound is not enolizable. At ambient temperatures, beta-hydroxy sulfides are produced^{1,2} but at 100°C the addition is followed by elimination to give a variety of olefinic products.^{64,65}

Additions to an active triple bond, such as in diphenyl acetylene, occurs in 95% yield to give 3-methylsulfinyl-1, 2-diphenyl-1-propene.⁶⁶ The dimsly ion adds to conjugated double bonds at ambient temperatures to afford sulfoxides.^{67,68} The addition to a wide variety of polymerizable monomers such as styrene, 4-vinylpyridine, acrylonitrile, methylmethacrylate, acrylamide, and ethylene oxide induces polymerization.^{53,59,70,71,72}

As a Carbon Methylating Agent

Adducts are initially produced when solutions of dimsly sodium in DMSO are heated with conjugated unsaturated compounds, such as butadiene, 1, 3-pentadiene,⁷³ polynuclear aromatic hydrocarbons or heterocycles^{74,75}, or systems such as stilbene or stilbazole.⁴⁸ The adduct eliminates sulfenic acid and rearranges bonds to produce methylated analogs of the starting hydrocarbons. Some yields are high, giving a useful way to accomplish carbon methylation.

As a Reducing Agent

The dimsly anion acts as a reducing agent in certain instances. It removes bromine or iodine from aromatic rings by reduction when a second halogen is present in the ortho position⁷⁶ and removes one bromine from certain gem-dibromocyclopropanes.^{77,78} The dimsly sodium solution in DMSO also donates an electron to nitrobenzene or nitrosobenzene to produce anion radicals.⁷⁹



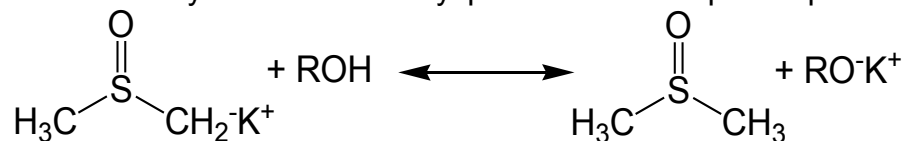
The DMSO anion is rapidly oxidized by the oxygen in air. This autoxidation can be prevented by the addition of 20% of t-butyl alcohol.⁸⁰ In this solvent mixture the concentration of dimsyl ion is greatly diminished with the equilibrium shifting in favor of the t-butoxide ion. This system is useful as a medium for the autoxidation of other compounds.

As an Oxidizing Agent

Although dimsyl sodium rarely behaves as an oxidizing agent, it does react with diphenylmethylsilane through the oxygen atom to give a quantitative yield of diphenylmethylsilanol.⁸¹

Dimsyl Sodium Solutions with Other Bases

Addition of an alcohol to dimsyl sodium or dimsyl potassium sets up an equilibrium:



which lies far to the right in favor of the alkoxide, leaving only a small amount of dimsyl ion.¹² The rate of proton exchange between t-butoxides and DMSO is very fast^{15,16} and if the dimsyl ion is consumed in a reaction, it can be rapidly replenished by shifting the equilibrium to the left. Thus several oxygen bases such as methoxide, ethoxide, isopropoxide t-butoxide can be used as a source of dimsyl ion in DMSO.⁸² The alkoxide-dimsyl ion-DMSO base systems can be just as effective as the dimsyl ion-DMSO system but they can be easier to prepare. Potassium t-butoxide which is quite soluble in DMSO has most commonly been used to generate the dimsyl ion by the addition of potassium t-butoxide to DMSO.^{83,58,84,53} Other bases, such as potassium hydroxide⁸⁵, phenoxide⁸⁶, tetraethylammonium hydroxide³ and tetraethylammonium fluoride⁸⁷ have also been found to generate a small amount of dimsyl sodium.

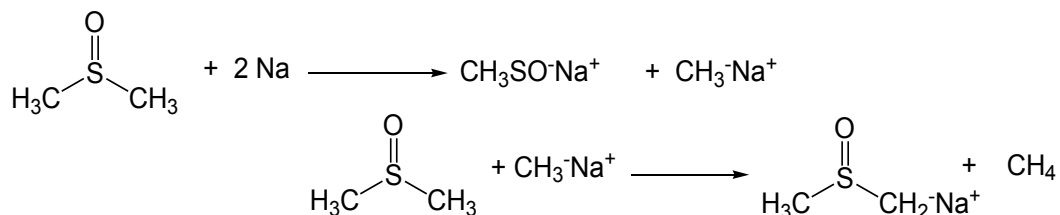
PREPARATION OF DIMSYL SODIUM

The dimsyl sodium solutions are easily prepared by stirring a mixture of sodium hydride in dry DMSO at 70-75°C until the reaction is complete. The DMSO anion reacts rapidly with water, carbon dioxide and oxygen. During formation, reaction and storage of dimsyl sodium these substances should be excluded as much as possible.

The procedure for preparing dimsyl sodium follows:

A mineral oil dispersion containing 48.0 g or 2.0 mole of sodium hydride was swirled three times in a round bottom flask with light petroleum ether to remove the oil (Notes 1, 2). The petroleum ether was decanted and sodium hydride was dried in a stream of dry nitrogen. The flask containing the dried sodium hydride was connected by means of a flexible tubing to a neck of a 4-necked flask containing well-stirred, dry DMSO (Note 3), 846 g. (770 ml or about 10.8 mole) under nitrogen. The DMSO flask was heated to about 60°C in a water bath and sodium hydride was introduced gradually by letting the hydride drop through the tubing. The addition rate held the temperature in the flask at 70-75°C (Note 4). The mixture was heated for a period of 45 min. after sodium hydride addition with vigorous stirring under a slow stream of nitrogen. Completion of the reaction is shown by the disappearance of sodium hydride and the cessation of hydrogen evolution (Note 5). The final solution was about 2.5 M in dimsyl sodium and was milky and grey-olive in color. The actual concentration of the dimsyl sodium can be assayed by titration with formamide using triphenyl methane as indicator.^{11,12}

For smaller scale preparations, e.g. 0.05 mole, the procedure of Corey and Chaykovsky can be used.² Instead of adding sodium hydride to DMSO, it is sometimes more convenient to add DMSO to the hydride. This is not recommended in larger scale (1 mole or greater) preparations. Addition of DMSO to sodium hydride can form lumps with heat dissipation problems. Forming the DMSO anion by directly reacting sodium or potassium with DMSO is not recommended. The principal reaction involves cleavage of the C-S bond which is followed by the reaction of the methyl sodium with DMSO to give the DMSO anion and methane rather than hydrogen as the evolved gas.⁸⁸



NOTES

1. It has been found that it is not always necessary to remove the mineral oil since it does not directly hinder the dimethyl sodium preparation. The removal is recommended where the mineral oil might complicate the isolation of the final product from the reaction mixture.

2. Particle size distribution of the sodium hydride influences reactivity.

3. DMSO is very hygroscopic and the industrial material always contains small quantities of water, 0.05-0.3%. It has been found in a number of dimethyl sodium preparations that it is not necessary to dry DMSO if a small quantity of sodium hydroxide can be tolerated. The amount of water in DMSO can be determined by gas chromatography using a 15" long column packed with Poropak S (50-100 mesh) with a helium flow of 50 ml/min.; column temperature 190°C, injector temperature 170°C, with the hot wire thermoconductivity detector at 220°C. A sample size of 30 microliters gives sufficient peak height without too much background. Water shows up immediately after the gases absorbed in DMSO. DMSO can be dried to about 10 ppm water or less by Linde molecular sieves (4Å, 14 x 30 mesh).

Distillation of DMSO produces a product with less than 200 ppm (0.02%) water. A convenient method of preparing near anhydrous DMSO for chemical reactions is to add 20% excess in a reaction vessel and vacuum distill (20-25 mm) the 20% DMSO slowly through a packed or Vigreux column leaving the dry DMSO in the vessel.

DMSO can also be dried by distilling it from calcium hydride at 4mm (b.p. 64°C).

4. The dimethyl sodium solutions are best prepared at temperatures of 70-75°C to obtain a sufficient rate of formation and a high yield. Higher temperatures should be avoided because the decomposition of dimethyl sodium becomes too rapid to be acceptable. Efficient stirring should be provided at all times during the reaction to avoid lump formation and local overheating.

5. After completion of the reaction, the solution should be cooled down rapidly prior to storage or use.

STABILITY

Carbanions in general have limited thermal stability and the dimethyl ion is no exception. Most applications of the dimethyl sodium solutions, such as proton removals, phosphorus ylide preparations or additions to carbonyl compounds occur at room temperature where thermal decomposition is not a problem. The DMSO anion reacts rapidly with water, carbon dioxide and oxygen. During formation, reaction and storage of dimethyl sodium these substances should be excluded as much as possible.



Decomposition Rates at Different Temperatures

a) Below 25°C

At temperatures of 25°C and lower, DMSO solutions of dimethyl sodium are quite stable. Sjöberg⁸⁹ found no decomposition when the solution was stored as a solid at 10°C for two months. At 20°C, Price and Whiting¹¹ found a decomposition rate of 8% per week. At 25°C, a 3 M solution of dimethyl sodium in DMSO decomposed at a steady rate of 3-4% per day as evidenced by the yield obtained when aliquot samples were reacted with benzophenone⁹⁰ (Figure 1). Although the decomposition of dimethyl sodium is exothermic, no temperature rise was observed when 3 M dimethyl sodium solution was stored one week at 25°C in a Dewar flask, i. e. the decomposition reaction was so slow that there were no problems of heat transfer.

b) At 40°C. -50°C.

As shown in Figure 1, dimethyl sodium decomposes at an appreciable rate at 40°C with 11% being lost in one day. A similar result was reported by Lyness, O'Connor and Berry⁴⁴ who observed a 9% loss in one day at 50°C.

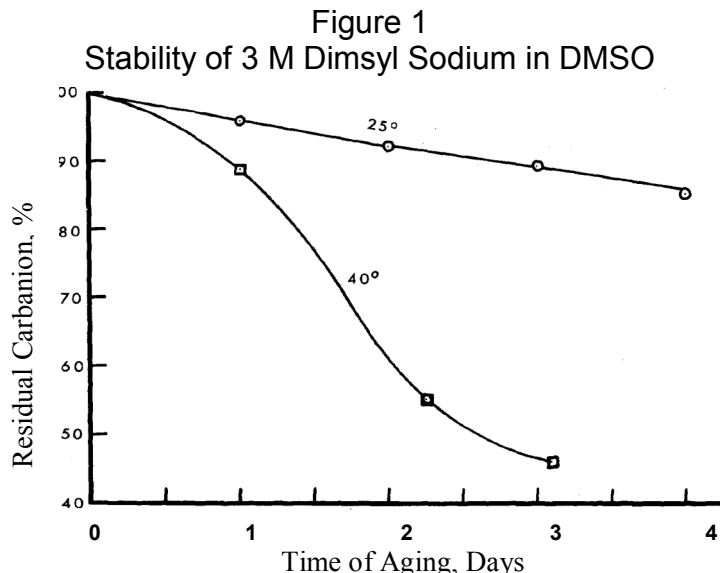
c) At 70°C. and Higher

Corey and Chaykovsky² pointed out that dimethyl sodium solutions are best prepared at temperatures of 70-75°C in order to obtain a sufficient rate of formation while avoiding the higher temperatures at which decomposition of dimethyl sodium is too rapid to be acceptable. Even at 70°C. the exothermic decomposition of dimethyl sodium is rapid enough to require some attention if this, or a higher temperature, is to be maintained for a length of time. However, as indicated above, most applications of the reagent are at room temperature where very little decomposition takes place.

d) Thermal Effects of Decomposition Reactions

The decomposition of dimethyl sodium is exothermic. At temperatures as low as 37°C., the decomposition of 3 M solution causes a considerable temperature rise if there is no heat removal. The temperature changes of 3 M solutions contained in a Dewar flask in ovens at 25°C, 37°C., and 45°C are shown in Figure 2. At initial temperatures above 25°C, some provision for heat removal is necessary to avoid undue temperature rise and acceleration of decomposition.

prolonged heating of dimethyl sodium solutions, adequate heat transfer and removal are needed at all times to avoid an uncontrolled temperature rise. The decomposition has been observed to be



explosive in glassware.^{91,92} It is our understanding that the explosions observed were caused by gas pressure generated during the uncontrolled exothermal decomposition.

2. Decomposition Reactions and Products

A number of reactions occur during the gradual thermal decomposition of dimsyl sodium and several of these have been recognized. Eighty-eight per cent of the dimsyl sodium (2.5 M solution in DMSO) was decomposed during five hours' heating at 70°C. Twenty-eight percent of the decomposed dimsyl sodium was accounted for as a 70:30 mixture of sodium methanesulfenate and sodium sulfide. These are the principal insoluble salts that accumulate during the decomposition. Both the dimsyl and methanesulfenate ions are destroyed during exotherms as shown in Figures 3 and 4.

Figure 2

Temperature Changes in 3M Dimsyl Sodium Solutions in Insulated Containers At Different Starting Temperatures

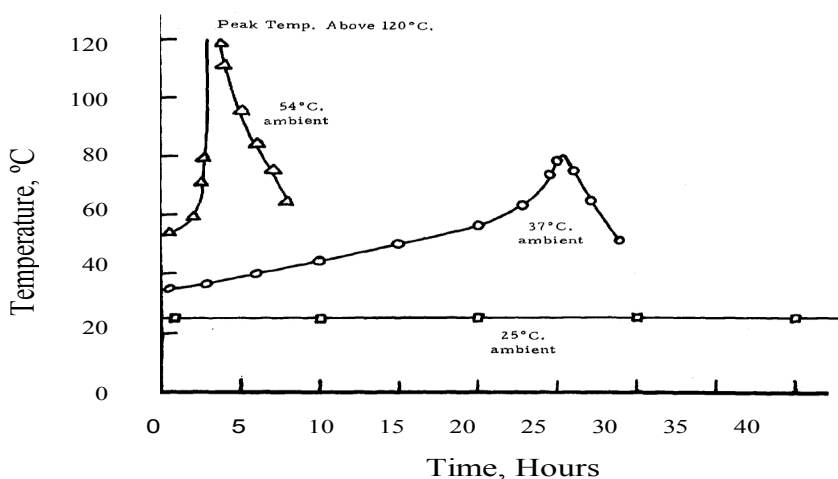


Figure 3 shows the thermal changes occurring when 7.5 mole of dimsyl sodium in DMSO solution (2.7 M) was stirred in a 3-liter glass flask immersed in a 71°C stirred water bath. The cooling effect of the bath was sufficient to control the temperature of the contents until the white precipitate, mainly sodium methanesulfenate, which gradually accumulated caused the mixture to gel. Effective heat transfer was lost at this point and an abrupt temperature rise occurred. At the peak of the temperature rise, the mixture was dark-brown and again became fluid. The dimsyl sodium was entirely decomposed at this time.

It should be pointed out that this rapid decomposition took place almost 3 hours after the sodium hydride addition to DMSO solution. In a usual dimsyl ion preparation, the reagent is stirred 30-45 minutes after the last NaH addition to complete the reaction. The solution would then be cooled from 70-75°C. to room temperature for most preparative or analytical applications.

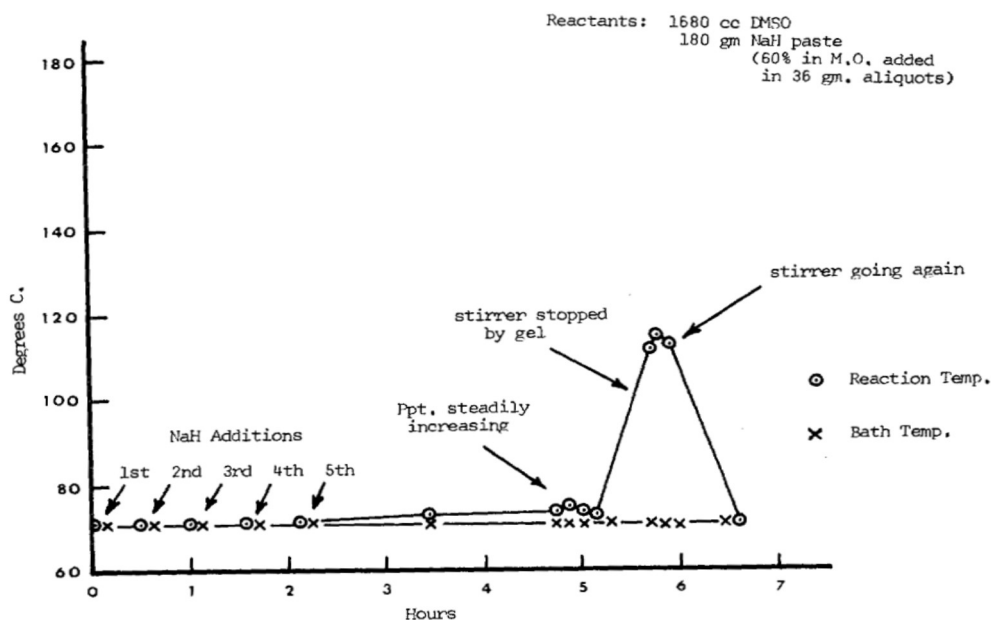
The exotherm was much greater when the bath temperature was increased to 85°C as soon as the formation of the reagent was completed (Figure 4). The resulting temperature rise after gellation was much more severe than that seen in Figure 3. When running those reactions which require prolonged heating of dimsyl sodium solutions, adequate heat transfer and removal are needed at all times to avoid an uncontrolled temperature rise. The decomposition has been observed to be explosive in glassware.^{91,92} It is our understanding that the explosions observed were caused by gas pressure generated during the uncontrolled exothermal decomposition.



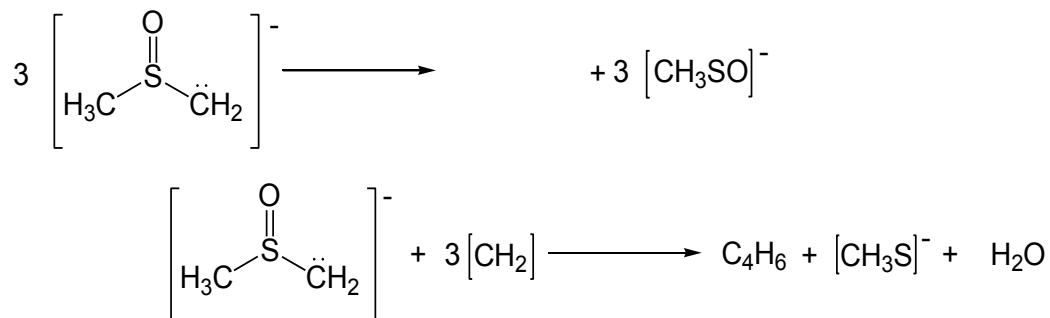
The fate of the methylene fragment was examined by Price and Yukuta⁹³ who accounted for 30% of the possible hydrocarbons as a mixture of conjugated dienes comprising:

- 40% 2, 4-dimethyl-1, 3-pentadiene
- 12% trans-3-methyl-1, 3-pentadiene
- 11 % trans-2, 4-hexadiene
- 11 % trans-1, 3-pentadiene
- 8 % isoprene
- 7 % 4-methyl-1, 3-pentadiene

Figure 3

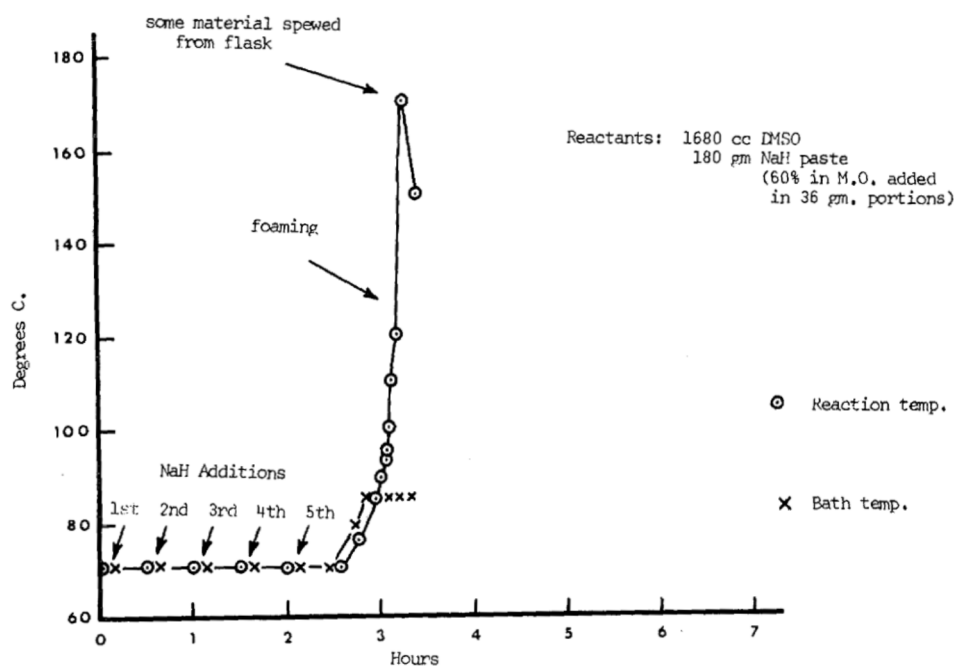


They suggested that butadiene may have been produced initially and was quickly methylated by dimethyl sodium. The stoichiometry of the initial decomposition can be shown as two steps:



After 150 hours at 100°C, methylsulfinates, methylsulfenates and methylthio anions were all present.

Figure 4
Thermal Changes of Dimethyl Sodium in DMSO Solution,
Raising Bath as Soon as NaH Has Reacted



GENERAL HANDLING AND SAFETY CONSIDERATIONS

a) Preparation

The procedure of Corey and Chaykovsky can be used to prepare the dimethyl sodium solution on a small scale, e. g. 0.05 mole.² A modification of this procedure involving pentane wash of the sodium hydride has been used to prepare dimethyl ion at kilo scale. The dimethyl sodium solutions are best prepared at temperatures of 70-75°C. Careful temperature control is required when operating dimethyl ion preparations at scale. It is advisable to monitor both the internal and skin temperatures of the reaction vessel. Higher temperatures should be avoided because decomposition of dimethyl sodium may become too rapid. *Efficient stirring should be provided at all times during the reaction of DMSO with sodium hydride.* The DMSO anion reacts with carbon dioxide, water, and oxygen.⁸⁰ During formation, reaction and storage of dimethyl sodium these substances should be excluded.²

b) Reactions

Most of the applications of dimethyl sodium are at lower temperatures where the thermal decomposition is not a problem. However, in those reactions in which concentrated solutions of dimethyl sodium in DMSO are to be heated for long times, the possibility of an exotherm needs to be recognized. Such an exotherm will be fueled both by the dissolved dimethyl sodium and at higher temperatures by the suspended sodium methanesulfonate, a decomposition product. It is thus advisable that adequate heat removal be maintained throughout the reaction. In addition to good agitation, it may sometimes be desirable to use more dilute solutions or to provide diluents to facilitate heat transfer from the slurry.



Another device that can be employed in some reactions is to use a base that will react with DMSO to provide only a small equilibrium concentration of dimsyl ion at any time. Potassium t-butoxide, tetraethyl ammonium hydroxide or anhydrous potassium hydroxide can sometimes be used this way.⁸² (See also the section on the 'Uses of the Dimsyl Ion Reagent Solution').

c) Storage

If it becomes necessary to store the dimsyl sodium solution for any length of time, this is best done below room temperature. There was no decomposition when the solution was stored as a solid at 10° C. for two months.⁸⁹ At 20°C., the decomposition rate is only about 8% a week.¹¹ At 40°C and higher, the decomposition rate becomes appreciable (about 9-11% a day at 40°C). This decomposition of dimsyl sodium is exothermic and it will cause a considerable temperature rise if fairly concentrated solutions (e. g. 3 M) are stored without provision for heat removal. Particular caution should be exercised with larger quantities of dimsyl sodium solutions. As previously mentioned, it is best to avoid storing large quantities of solutions more concentrated than 2 M.

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