

benzophenone, triphenylmethane, triphenylmethanol, and magnesium bromide hexahydrate in amounts corresponding to their per cent yields given in Table I. To this mixture was added 1.00 g (0.0167 mol) of acetic acid and 0.508 g (0.0065 mol) of DMSO. Nmr peak area integration gave an average DMSO/acetic acid ratio of 23:18. Thus, only 62.4% of the acetic acid remained in the aqueous layer. An average of three different determinations, each of slightly different volumes of two liquids, resulted in an average partition coefficient (ether/aqueous) of $0.38/0.62 = 0.61$, which indicates that acetic acid preferentially remains in the aqueous layer by a factor of $0.62/0.38 = 1.63$.

Reaction of Acetic Acid with Phenylmagnesium Bromide (1:2:3 Molar Ratio).—Acetic acid (1.0 g, 0.0167 mol) was slowly added to 0.035 mol of phenylmagnesium bromide (2) in 50 ml of anhydrous ether. The reaction mixture was stirred for 3 hr, cooled, and hydrolyzed with cold 6 *N* hydrochloric acid. Analysis of the organic layer was accomplished by glpc analysis. The following products were found: benzene, phenol, acetophenone, biphenyl, 1,1-diphenylethanol, and 1,1-diphenylethene. The alkene is apparently formed by dehydration of part of the tertiary alcohol. Acetophenone was found to be present ($15 \pm 1\%$ yield based on the acid), and the combined quantities of the tertiary alcohol and 1,1-diphenylethene amounted to about $40 \pm 1\%$ (based on the acid). Standard solutions were used to check each of these compounds. These yields are not unreasonably low when one considers that 1 mol of the Grignard reagent was destroyed by the acidic proton of acetic acid.

Reaction of Trityl Bromide with Phenylmagnesium Bromide (2) and Oxygen.—Phenylmagnesium bromide (0.0121 mol) was added to a reaction vessel along with 50 ml of anhydrous ether.

Then 3.0 g (0.0093 mol) of trityl bromide dissolved in anhydrous ether was added dropwise. After 1 hr, the reaction mixture was dark orange-red color, but no solid material had formed. At this time, oxygen was introduced into the reaction mixture and a solid began to form. After 6 hr, the reaction mixture had assumed a pale yellow color and trityl peroxide (7) was readily visible. The reaction mixture was cooled in an ice bath and then hydrolyzed with 40 ml of ice-cold 6 *N* hydrochloric acid; yield of trityl peroxide was 47% (1.10 g, 0.00212 mol). Other products observed by glpc analysis were benzene, phenol, acetophenone (11%), biphenyl, benzophenone (17%), triphenylmethane (26%), triphenylmethanol (7%), and tetraphenylmethane (3%). A solution of trityl bromide in ether was bubbled with dry O₂ for 6 hr. The solution remained unchanged and no trityl peroxide precipitated.

Registry No.—Trityl acetate-¹⁸O, 20449-05-2; phenylmagnesium bromide, 100-58-3.

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The Thermal Decomposition of Dimsyl Ion in Dimethyl Sulfoxide

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The decomposition of sodium dimsyl in dimethyl sulfoxide at temperatures above 80° produces a mixture of methylated butadienes and a white precipitate which, by titration and reaction with benzyl chloride, is evidently a mixture of sodium methanesulfenate, sodium methanesulfinate, and sodium methylmercaptide.

One of the useful strong bases in dimethyl sulfoxide (DMSO) is its anion, first prepared by Corey and Chaykovsky.² These authors mentioned the thermal decomposition of this reagent and it was the purpose of this investigation to establish the nature of the reactions involved.

When *ca.* 1 *M* solutions of sodium dimsyl are heated to 80° for several hours, the solutions turn dark red-brown, a voluminous white precipitate separates, and a volatile product and an extremely foul odor are evolved. The initial reaction can become violent at temperatures above 100°.

The volatile products have been collected by trapping at -78° and separated by gas chromatography. Many of the fractions were identified unequivocally by comparison of their nmr and mass spectra with those reported for methylated butadienes. Typical examples are summarized in Table I.

The nmr spectrum of peak 1 indicates that it is *not* butadiene; it shows mainly paraffinic proton resonance in four major peaks between δ 1.3 and 1.85 with only very weak absorbance in the olefinic proton 5-6 region. This material is probably from residual petroleum ether used to wash sodium hydride free of mineral oil. The other peaks identified as methylated butadienes gave ex-

TABLE I
IDENTIFICATION OF GLPC FRACTIONS FROM VOLATILE LIQUID
FROM SODIUM DIMSYL DECOMPOSITION

Peak No.	Wt %		Mass	Identity
	A ^a	B ^b		
1	6.4	0.9
2	8.4	1.9	C ₅ H ₈	Isoprene
3	11.0	15.2	C ₆ H ₈	<i>trans</i> -1,3-Pentadiene
4	0.3	4.2
5	0.2	1.6	C ₂ H ₆ S	Dimethyl sulfide
6	11.8	16.3	C ₈ H ₁₀	<i>trans</i> -2-Methyl-1,3-pentadiene
7	6.6	12.5	C ₆ H ₁₀	4-Methyl-1,3-pentadiene
8	11.0	16.6	C ₆ H ₁₀	<i>trans</i> -2,4-Hexadiene
9	40.0	28.2	C ₇ H ₁₂	2,4-Dimethyl-1,3-pentadiene

^a Decomposed for 5 hr at 85°, 33% total yield of hydrocarbons.

^b Decomposed for 7.5 hr at 78°, 27% total yield of hydrocarbons.

cellent nmr spectra with chemical shifts, splitting constants, and peak heights identical with authentic spectra.

A number of sulfur ylides have been reported to be sources of ethylene and/or polymethylene, although the exact mechanism of the conversions and whether they involve methylene as an intermediate are matters of controversy.³ The formation of dienes from a methylene donor, however, appears to be a unique reaction for

(1) Supported in part by National Science Foundation Grant GP-5269. From the Ph.D. Dissertation of T. Yukuta, University of Pennsylvania, 1968.

(2) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **84**, 866 (1962).

(3) A. W. Johnson, "Ylid Chemistry," Academic Press Inc., New York, N. Y., 1966, p 304.

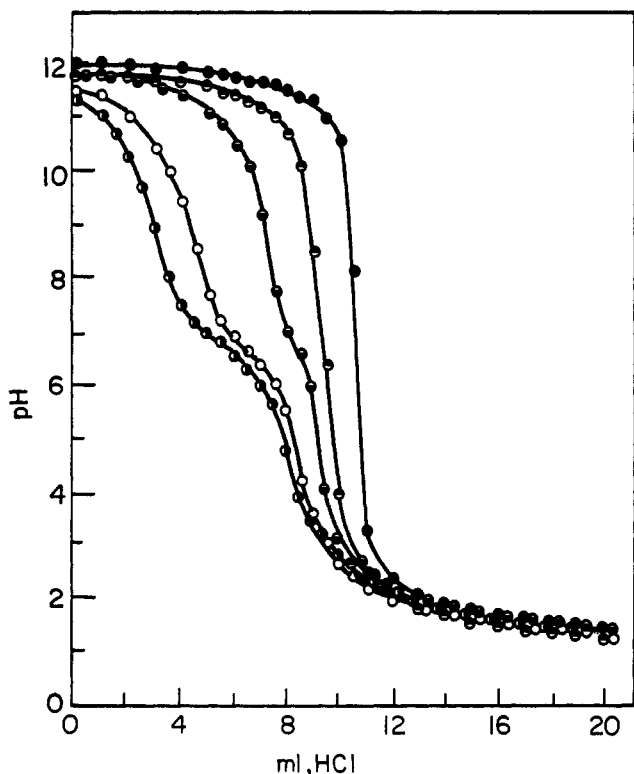
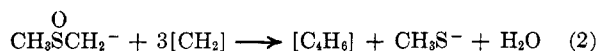
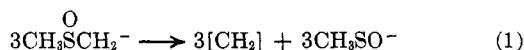


Figure 1.—The titration with 0.1 *N* hydrochloric acid of dimethyl sulfoxide solutions decomposed at 97° for 0.0 (●), 0.5 (◐), 5 (◑), 113 (○), and 211 (◒) hours.

“methylene” generated from dimethyl anion. In this case, the over-all reaction requires an oxidative step, and the stoichiometry can be represented by eq 1 and 2.



The formation of methylene dimer and polymer from neutral ylides has been postulated by some³ to proceed through direct exchange of methylene between ylides³ without intervention of “free” methylene. Such a course in this instance seems even less likely because it would require bimolecular reaction of two anions.

The failure to isolate any butadiene is readily explained by its rapid reaction with dimethyl sulfoxide, while further alkylation of 1,3-pentadiene under the same conditions required 17 hr. It can be assumed that the intermediate nucleophilic attack by dimethyl sulfoxide on the dienes would be still further hindered by introduction of two or three methyl groups. The considerable increase in branched-chain butadienes in our experiments may be due either to intervention of “free” methylene in addition to dimethyl sulfoxide ion itself as alkylating agent at the higher temperatures used, or to rearrangement or methylene insertion in the unknown intermediates in eq 2 of the thermal decomposition reaction.

By reaction of the decomposition mixture with benzyl chloride, 50–60% of the sulfur of decomposed dimethyl anion was recovered in the reduced sulfide state, while

about 10–12% was recovered as sulfoxide and sulfone. This leads to the conclusion that the sulfenolate ion may disproportionate under the conditions employed by us, even though O'Connor and Lyness⁵ report sodium methanesulfenolate to be stable in dimethyl sulfoxide for an hour at 30–40°. The relatively low yields of the



sulfoxide and sulfone we ascribe at least in part to losses in the eight washings of product with salt water, necessary to remove dimethyl sulfoxide. The formation of benzyl sulfide, sulfoxide, and sulfones from decomposed dimethyl sulfoxide solutions is in marked contrast to the formation of *trans*-stilbene (which we have confirmed) as the main product from fresh dimethyl sulfoxide solutions.⁶

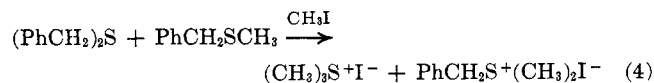
Addition of water and then titration with hydrochloric acid (Figure 1) indicates that the single strong base initially present is converted to the three weaker dimethyl sulfoxide insoluble bases of eq 3 with very nearly a statistical redistribution of oxygen. After 211 hr at 97°, when iodimetric titration (Table II) indicated 92% total conversion to the three species in eq 3, the p*K*_a titration indicated 26% of the base has p*K*_a = 2.9, 52% has p*K*_a = 6.7, and 23% has p*K*_a = 10.7. A p*K*_a of about 11 for CH₃S would be in reasonable accord with the p*K*_a of 11.5 reported for butyl mercaptan⁷ and the p*K*_a of butanesulfinic acid is reported to be 2.1.⁸ This leaves some question about the acid titrating with a p*K*_a near 7, but it does seem reasonable that the p*K*_a of a sulfenic acid would be intermediate between its reduction and oxidation products.

TABLE II
IODIMETRIC TITRATION OF SODIUM DIMETHYL SULFOXIDE SOLUTION
DECOMPOSED AT 97°

Heating time, hr	0	0.5	5	113	211
ml of 0.1 <i>N</i> HCl to pH 6	11	10	9	7	6
ml of 0.13 <i>N</i> I ₂	0.30	1.40	4.80	6.30	7.40
Mequiv/mol of dimethyl sulfoxide	0.037	0.173	0.59	0.78	0.91

If the titration data indeed accurately reflect the equilibrium in eq 3, then the isolation of a 50–60% yield of sulfide from the benzyl chloride reaction could be explained by the reasonable postulates that (a) mercaptide ion is a more reactive nucleophile than sulfenolate, and (b) the disproportionation reaction (eq 3) is fast compared with the reaction of sulfenolate with benzyl chloride.

In addition to benzyl methyl sulfide and sulfone, two other major products isolated from benzyl chloride reactions deserve comment. One is dibenzyl sulfide, which normally was isolated in the same chromatogram fraction as benzyl methyl sulfide. The ease with which this mixed sulfide fraction is converted to trimethylsulfonium ion by methyl iodide suggests that a somewhat



similar disproportionation may explain the presence of dibenzyl sulfide. The volatility of methyl chloride may

(5) D. E. O'Connor and W. I. Lyness, *ibid.*, **30**, 1620 (1965).

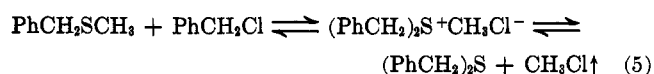
(6) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **84**, 3782 (1962); **87**, 1353 (1965).

(7) W. H. Fletcher, *ibid.*, **68**, 2726 (1946).

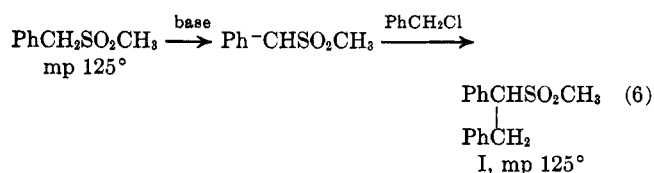
(8) P. Rumpf and J. Sadet, *Bull. Soc. Chim. Fr.*, 450 (1958).

(4) P. A. Argabright, J. E. Hofmann, and A. Schriesheim, *J. Org. Chem.*, **30**, 3233 (1965).

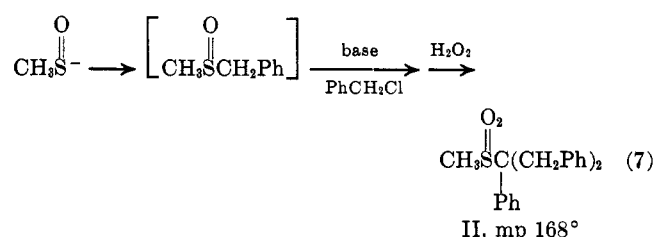
indeed promote shift of these equilibria toward dibenzyl sulfide.



A second type of product is illustrated by the isolation of the sulfone I, which is presumably formed by the base-catalyzed further benzylation of benzyl methyl sulfone. The bisbenzyl sulfone (II) was also isolated



and identified, although it appears to have been obtained in the reaction mixture first as the sulfoxide. Presumably a second alkylation of I was hindered by the two sulfone oxygens, whereas the analogous sulfoxide readily alkylated a second time. Generally speaking,



these further benzylated products were obtained from benzyl chloride treatment of short-time decompositions, when undecomposed dimsyl ion would remain as the strong base necessary to remove the benzyl proton α to the sulfone or sulfoxide.

The nmr spectra of I and II show that the two benzyl hydrogens are in different environments. For the case of I, the benzyl hydrogens appear at δ 3.42 and 3.84, splitting each other by $J = 13.8$ cps. Each is also split by the adjacent methine hydrogen (δ 4.57) by $J = 10.2$ and 4.8 cps, respectively. For the case of II, the benzyl hydrogens appear as two doublets, δ 3.57 and 3.87, with $J = 15.0$ cps.

Preliminary experiments attempting to treat decomposed dimsyl solutions with methyl iodide led to the isolation of beautiful needles of $\text{NaI} \cdot 2\text{CH}_3\text{SOCH}_3$, mp 147° , recrystallizable from ethanol.

Experimental Section

Elemental analyses were performed by A. Bernhardt, Micro-analytical Laboratory, Ruhr, Germany, and Galbraith Laboratories, Inc., Knoxville, Tenn. The melting points of all crystalline compounds were uncorrected.

Volatile Hydrocarbons.—A 3.75-g sample of a 50% dispersion of sodium hydride in oil was placed in a 100-ml flask and washed three times by decantation with low-boiling petroleum ether. After evaporation by water aspirator, 40 ml of redistilled dimethyl sulfoxide was added by syringe. The reaction mixture was cautiously heated to 75° until gas evolution ceased. A liquid collector trap, cooled in Dry Ice-acetone, was attached and the solution was heated cautiously to 80 – 85° and held there for 5 hr. The trap contained 364 mg of liquid, which was separated by preparative gas chromatography in a $20 \text{ ft} \times \frac{3}{8}$ in. column packed with 30% Carbowax 20M maintained at 65° . The results of two such fractionations are shown in Table I.

The identity of fraction 5 as dimethyl sulfide was indicated by the mass spectrum, which showed major peaks for CH_3S^+ (relative intensity 100), $(\text{CH}_3)_2\text{S}^+$ (82), CH_3S^+ (50), H_3S^+ (42), and C_2H_3^+ (28).

Acid-Base Titration.—A pale blue-green 1.05 *M* solution of sodium dimsyl in dimethyl sulfoxide, prepared as above, was divided into 1-ml aliquots, sealed in nmr tubes and heated to 97° for a specified time, cooled, and diluted with 40 ml of water prior to titration with 0.1 *N* HCl. The results are summarized in Figure 1.

Iodine Titration.—Similar 1-ml aliquots, heated in the same way and then dissolved in 40 ml of water, were titrated with 0.13 *N* iodine solution (after neutralization to pH 6 by 0.1 *N* HCl) using starch indicator. The results are summarized in Table II.

Test for Solvent Participation.—Decomposition mixtures of sodium dimsyl run for times as long as 336 hr at 105° were added to $^2\text{H}_2\text{O}$ and dioxane. Comparison of the dimethyl sulfoxide peak with the dioxane peak indicated no significant change in dimethyl sulfoxide over this interval, indicating that the decompositions observed were indeed those of the dimsyl ion.

Reaction of Decomposed Dimethyl with Benzyl Chloride. A.—A solution of 0.10 mol of sodium dimsyl in 50 ml of dimethyl sulfoxide was decomposed thoroughly by heating for 150 hr to a maximum of 105° . After cooling, 12.7 g (0.1 mol) of benzyl chloride was added dropwise over 10 min with stirring in a water bath to control the initial exothermic reaction. After 20 min, a 45° oil bath was placed around the reaction mixture, which was stirred at this temperature for 16 hr to yield a viscous dark brown solution.

The contents were poured into 250 ml of ether to give a precipitate which was filtered and washed with a total of 800 ml of ether to afford 6.81 g of powder (theory for NaCl, 5.85 g) after drying under vacuum. The ether solution was washed with 250 ml of NaCl-saturated water eight times in order to remove dimethyl sulfoxide, giving a dark brown solution which was dried over anhydrous sodium sulfate. Evaporation of ether with a rotary evaporator gave 13.31 g of viscous dark red-brown liquid with some crystalline solids.

The 13.31 g of oily liquid was dissolved in benzene and submitted to column chromatography with benzene and then methanol as eluents (column: 4×33 cm, 80–200 mesh A-540 Fisher alumina). Three main fractions were obtained as follows: i, 11.20 g (viscous dark red-brown liquid, from which small amounts of needle crystals separated); ii, 0.35 g (pale yellow solid); and iii, 1.27 g (by flushing with absolute methanol, dark red-brown liquid, from which needle crystals separated); recovery 96.3%.

A solution of 3.36 g of i in 50 ml of glacial acetic acid was treated with 10 ml of 50% H_2O_2 dropwise, producing an exothermic reaction. After several days, the contents were poured into 150 ml of water and extracted three times with 200 ml of ether. The combined extracts were washed three times with 200 ml of water and twice with 200 ml of 10% aqueous K_2CO_3 , dried (anhydrous Na_2SO_4), and evaporated, leaving 3.00 g of pale yellow crystalline solid, mp 90 – 130° . Recrystallization from 95% ethanol gave dibenzyl sulfone as colorless needle crystals, mp 148 – 150° (lit. m 150°), nmr (CF_3COOD) δ 7.44 (s, 5 H) and 4.43 ppm (s, 2 H). The evaporation of solvent left a crystalline yellow-tinged powder, mp 115 – 118° (hot CCl_4), identified by nmr spectra in CF_3COOH as methyl benzyl sulfone.

The nmr spectrum of i indicated that it was a mixture of dibenzyl sulfide (61.2 mol %) and methyl benzyl sulfide (38.8 mol %). The nmr spectrum of crystals, obtained by oxidation of i, before recrystallization (*i.e.*, mp 90 – 130°) showed that it was a mixture of dibenzyl sulfone (76.4 mol %) and methyl benzyl sulfone (23.6 mol %).

Recrystallization of ii gave colorless needle crystals of methyl benzyl sulfone, mp 123 – 125° (95% ethanol) (lit.⁹ mp 125 – 127°). The nmr spectrum in CF_3COOD showed bands at δ 7.48 (s, 5), 4.53 (s, 2), 3.03 (s, 3), and in $\text{DMSO}-d_6$ at 7.44 (s, 5), 4.49 (s, 2), and 2.91 ppm (s, 3).

The decantation of the supernatant from iii yielded 0.10 g of white needle crystals, mp 123 – 125° (95% ethanol), identified as methyl benzyl sulfone. The ir spectrum (infrared, neat) of the filtrate showed strong sulfoxide stretching absorption at 1020 cm^{-1} .

B.—Following the same procedures as above but for dimsyl solution decomposed only 7.5 hr at 78° , benzyl chloride (12.90 g, 0.10 mol) was added to the viscous red-brown solution. Stirring was continued for 13 hr at 42 – 44° . After filtering, washing with ether, and evaporation, 6.66 g of powder (theory for NaCl, 5.85

(9) T. R. Lewis and S. Archer, *J. Amer. Chem. Soc.*, **73**, 2109 (1951).

g), and 13.71 g of viscous red-brown liquid were obtained. From the latter, crystalline needles separated on standing.

The entire 13.20 g of the liquid containing some needle crystals was dissolved in benzene and submitted to column chromatography as above to afford three main fractions using benzene and then methanol as an eluent: i, 9.00 g (red-brown liquid), ii, 0.18 g (light brown liquid), iii, 3.06 g (by flushing with absolute methanol, viscous dark brown liquid); recover 95.9%.

From the nmr spectrum of i (CCl₄), δ 7.21 and 7.16 (broad, 12.2), 4.42 (s, 0.7), 3.49 and 3.44 (s, 2.9), 2.04 (s, 1.9), and 1.79 ppm (s, 2.0), the composition of the mixture was estimated as dibenzyl sulfide (28.6 mol %), methyl benzyl sulfide (46.4 mol %), and unreacted benzyl chloride (25.0 mol %).

Fraction i (3.22 g) was dissolved in 4 ml of absolute ethanol, and 3 ml of methyl iodide was added. After standing at room temperature overnight, white needle crystals separated from the dark red-brown supernatant. Another 1 ml of methyl iodide was added, and the fraction was left overnight again. The fine white needles were filtered and washed with absolute ethanol to yield 2.35 g of trimethylsulfonium iodide, mp 209–215° with sublimation (95% ethanol) (lit.¹⁰ 203–207°), nmr (D₂O) δ 2.92 ppm (s). The nmr and ir spectra were identical with those reported for trimethylsulfonium iodide.¹⁰

To the dark red-brown mother liquid, ether was added to yield white needle crystals. A total of 800 ml of ether was used until no further precipitate occurred to give 1.15 g of the crystals, identified as dimethylbenzylsulfonium iodide. Recrystallization afforded flat needles: mp 99–101°; nmr (D₂O) δ 7.57 (s, 5 H), 4.61 (s, 2 H), and 2.83 ppm (s, 6 H).

Anal. Calcd for C₉H₁₃SI: C, 38.58; H, 4.69; I, 45.29; S, 11.45. Found: C, 38.63; H, 4.82; I, 45.36; S, 11.61.

After solvent evaporation, the mother liquid afforded 2.79 g of highly lachrymatory dark red-brown liquid, which was not further studied (presumably benzyl iodide).

(10) R. Kuhn and H. Trischmann, *Ann. Chem.*, **611**, 117 (1958).

A 3.06-g sample of iii was dissolved in CCl₄ to give white needle crystals on standing (0.92 g). Solvent evaporation and addition of 95% ethanol gave an additional 0.83 g of the crystals. Recrystallization afforded white wooly needle crystals of methylsulfonylbzylphenylmethane (I), mp 120–122° (CCl₄).

Anal. Calcd for C₁₅H₁₆SO₂: C, 69.18; H, 6.21; S, 12.31. Found: C, 69.06; H, 6.21; S, 12.47.

The mother liquid was condensed to give 1.24 g of red-brown liquid (showing sulfoxide by ir) which was dissolved in 30 ml of glacial acetic acid and oxidized with 6 ml of 50% H₂O₂ to yield 1.00 g of yellow oily solid. Recrystallization gave white needle crystals of methylsulfonyldibenzylphenylmethane (II), mp 165–168° [95% ethanol, followed by petroleum ether (bp 60–110°)–CHCl₃].

Anal. Calcd for C₂₂H₂₂SO₂: C, 75.38; H, 6.34; S, 9.15. Found: C, 75.38; H, 6.37; S, 9.16.

Reaction of DMSO with NaI.—By heating for 39 min at 80°, 6.10 g of NaI was dissolved in 40 ml of redistilled dimethyl sulfoxide. No precipitate appeared on standing at room temperature for a week. However, when the concentration was higher, e.g., 10 g of NaI in 40 ml of dimethyl sulfoxide, colorless crystals appeared. The solution was poured into 100 ml of benzene to yield 13.71 g (theory, 12.5 g) of white solid after filtration under N₂. Recrystallization from absolute ethanol afforded hygroscopic white needles, mp 144–147°.

Anal. Calcd for C₄H₁₂IONaS₂: C, 15.69; H, 3.96; I, 41.45; Na, 7.51; S, 20.94. Found: C, 15.56; H, 3.79; I, 41.50; Na, 7.41; S, 20.75.

Registry No.—Dimesyl ion, 13810-16-7; dimethyl sulfoxide, 67-68-5; I, 15733-05-8; II, 20505-04-8; methyl benzyl sulfone, 3112-90-1; NaI·2CH₃SOCH₃, 4659-76-1; dimethyl benzyl sulfonium iodide, 20483-21-0.

The Thermal Decomposition of β -Hydroxy Ketones

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β -Hydroxy ketones decompose thermally to mixtures of aldehydes and ketones in a reaction that is the reverse of the aldol condensation. A study has been carried out of the kinetics of the thermal decomposition of some β -hydroxy ketones in xylene solution. The results indicate that the reaction is unimolecular and involves a cyclic transition state. Comparison of the rates of decomposition of the different β -hydroxy ketones indicates that little charge separation is obtained during the breaking of the carbon-carbon bond in the transition state.

β -Hydroxy ketones decompose thermally¹ to give mixtures of aldehydes and/or ketones in a reaction which is the reverse of the aldol condensation. A kinetic study of the pyrolysis of 4-hydroxy-4-methyl-2-pentanone in the gas phase² showed that the decomposition is homogeneous and follows first-order kinetics, and it was proposed that the reaction involves a six-membered cyclic transition state. As a further test of this mechanism, we have carried out a study of the products and kinetics of the thermal decomposition of 4-hydroxy-4-methyl-2-pentanone in dilute xylene solution. It would be expected³ that, if in the gas phase the pyrolysis of 4-hydroxy-4-methyl-2-pentanone does involve a cyclic intramolecular mechanism, the same reaction carried out in nonpolar solvent would involve a similar type of mechanism, thus giving rise to similar products and first-order kinetics.

Furthermore, no kinetic measurements have been carried out for the thermal decomposition of other β -hydroxy ketones.

We have therefore studied the kinetics of the thermal decomposition of 4-hydroxy-3-methyl-2-pentanone and 4-hydroxy-2-pentanone, in order to examine the influence of the differently substituted methyl groups on the mechanism and velocity of pyrolysis.

Discussion

Quantitative analysis, using gas-liquid chromatography, of the products of the thermal decomposition of 4-hydroxy-4-methyl-2-pentanone in dilute xylene solution showed that acetone is by far the principal product of the reaction, being obtained in a yield of >95%, although a small amount (<5% in total) of two other unidentified products was also observed.

The rate of decomposition of the 4-hydroxy-4-methyl-2-pentanone was followed using glpc, by measuring both the rate at which acetone is formed and the rate of disappearance of the 4-hydroxy-4-methyl-2-pentanone.

(1) C. D. Hurd, "The Pyrolysis of Organic Compounds," The Chemical Catalog Co., Inc., Reinhold Publishing Corp., New York, N. Y., 1929, p 164.

(2) G. G. Smith and B. L. Yates, *J. Org. Chem.*, **30**, 2067 (1965).

(3) S. W. Benson, "The Foundation of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 508.