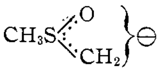
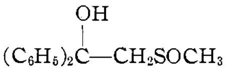
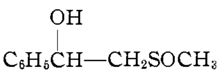


I



$(C_6H_5)_2C(OH)—CH_2SOCH_3$

II



$C_6H_5CH(OH)—CH_2SOCH_3$

III

The methylsulfinyl carbanion is strongly basic as is shown by its rapid reaction with triphenylmethane to produce a deep red solution of triphenylcarbanion. An approximate equilibrium constant for this reaction was determined by deuteriation of mixtures from known amounts of the starting reagents with excess deuterium oxide and measurement of the ratio triphenylmethane: triphenylmethane-d_1

$$K_{\text{eq}} = \frac{[(C_6H_5)_3C^-][CH_3SOCH_3]}{[CH_3SOCH_2^-][(C_6H_5)_3CH]} = 21 \pm 4\ (25°)$$

Equilibrium for this proton transfer is attained in less than 15 minutes at 25°.

The reactivity of I is sufficient to effect the conversion of phosphonium salts to ylides thereby permitting an extremely simple and convenient modification of the Wittig reaction. Thus, the interaction of sodium methylsulfinylcarbanion with one equivalent of ethyl triphenylphosphonium bromide at room temperature led to formation of ethylidenetriphenylphosphorane as shown by color change and by the reaction with benzophenone (0.85 equivalent) to give 1,1-diphenylpropene-1, m.p. 49°,[4] in 97.5% yield after 3 hours at 25° and 1.5 hours at 60°.

Chlorobenzene reacts at room temperature with an excess of sodium methylsulfinyl carbanion (6.7 equivalents) with spontaneous evolution of heat to yield methyl benzyl sulfoxide, m.p. 55–56°[5]; when a smaller excess (2.5 equivalents) of the anion is employed considerable amounts of methyl benzhydryl sulfoxide, m.p. 115–116°, result. In view of the strongly basic nature of the carbanion it is quite possible that substitution occurs *via* benzyne, in which case applications of I in this area can be envisioned.

We have not as yet had occasion to study the base-catalyzed generation of other types of reactive species, *e.g.*, carbenes, with this system. However, it might be noted that the reaction of benzyl chloride with sodium methylsulfinyl carbanion at room temperature produces *trans*-stilbene as the major poduct (together with an oily mixture of sulfoxides).

In spite of the high reactivity of the anion I in carbonyl addition as evidenced by the rapid formation of II from benzophenone, reaction with enolizable ketones seems to occur preferentially by proton transfer affording enolates which are stable to further attack by the reagent, the starting ketone being recovered unchanged after acidification. Such proton transfer predominates heavily with desoxybenzoin, cyclohexanone, 4-phenylcyclohexanone and norcamphor but to a lesser extent with camphor, which affords substantial amounts (28%) of carbonyl addition product (as a mixture of isomers, m.p. 94–130°).

The fact that the anion I is even more basic than trityl anion together with the recently published findings that base-catalyzed reactions occur at greatly enhanced rates in dimethyl sulfoxide as solvent[6,7] can be taken as an indication of the potency of the methylsulfinyl carbanion-dimethyl sulfoxide system. Further studies of I and also of some other sulfinyl carbanions are in progress.

We are indebted to the National Institutes of Health for a grant which supported this work.

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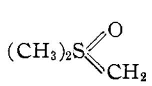
DIMETHYLSULFOXONIUM METHYLIDE

Sir:

We have observed that the readily accessible trimethylsulfoxonium halides[1,2] (I) undergo proton transfer to strong base with formation of a reactive substance of considerable utility in synthesis which can reasonably be formulated as dimethylsulfoxonium methylide (II) on the basis of chemical data.

$(CH_3)_3\overset{+}{S}=O\ X^-$

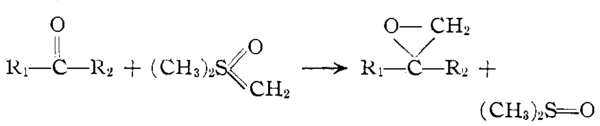
I



II

Solutions of II in dimethyl sulfoxide were prepared from the iodide or chloride I by stirring with one equivalent of powdered sodium hydride under nitrogen at room temperature (rapid evolution of hydrogen, exothermic). The ylide II also can be obtained in tetrahydrofuran by reaction of the more readily soluble chloride I in that solvent with powdered sodium hydride at reflux.

One of the most striking properties of II is its reactivity toward ketones and aldehydes which in many instances takes the form



Epoxides have been produced by this process from benzophenone (90%), 4-phenylcyclohexanone (72%), cycloheptanone (71%) and benzaldehyde (56%). Most of these reactions were carried out with a small excess of II at 25° for one hour, then a further hour at 50°.[3] Certain ketones appear resistant to the transformation, in particular desoxybenzoin and Δ^4-cholestenone, probably as a consequence of an enhanced tendency to form enolate ions by proton transfer to II.[4]

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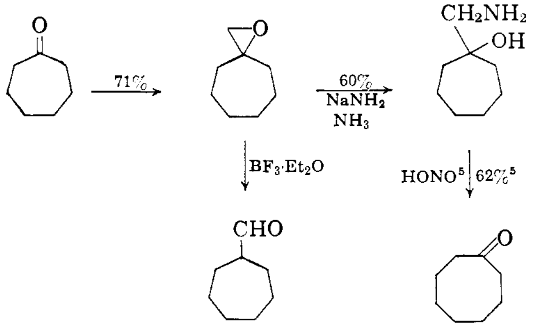
[3] Satisfactory analytical data were obtained on all products described herein.

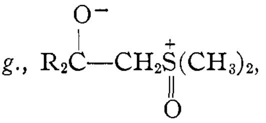
[4] Such resistance to epoxide formation may disappear under other conditions, a point now under investigation. However, it may prove useful in cases where selectivity is required.

It is clear that at least in certain instances the reaction of II with a ketone is the most practical method for synthesis of the corresponding epoxide and that this, in turn, provides useful routes to other structures. For example, these transformations have now been established from cycloheptanone (yields given are probably not optimal)



91% (as 2,4-dinitrophenylhydrazone)

A different mode of reaction results in systems which are susceptible to Michael addition as illustrated by benzalacetophenone which reacts with II to form 1-phenyl-2-benzoylcyclopropane[6] (95% yield) and only minor amounts of the epoxide derived from carbonyl addition. Such reactions represent a promising method for carbocycle synthesis.

The methylide II probably is an intermediate in the base-catalyzed hydrogen–deuterium exchange previously observed[7,8] with I iodide. The fast rate of this exchange[7] and our own observations indicate that the ylide is quite stable; we are now engaged in chemical and physical studies aimed at defining the structure of sulfoxonium ylides and their reactivity in more detail. Whether methylene transfer from dimethylsulfoxonium methylide to unsaturated linkages occurs *via* an intermediate addition product, *e.g.*,  $R_2\overset{O^-}{\overset{|}{C}}—CH_2\underset{\underset{O}{\|}}{\overset{+}{S}}(CH_3)_2$, or by a direct route is not known at present. This point is also under investigation.

This work was supported by a grant from the National Institutes of Health.

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ON THE TWO FORMS OF HYDROGEN ATOMS IN NEUTRAL SOLUTIONS IRRADIATED BY X-RAYS

Sir:

Recently, data have been obtained[1-8] which indicate that most of the "H" atoms produced in irradiated aqueous neutral solutions are probably electrons. The results of Allan and Scholes[2] indicate that H atoms are produced in irradiated solutions by:

$$e_{aq} + H_3O^+ \longrightarrow H + H_2O \qquad (1)$$

and react with organic scavengers (*e.g.*, 2-propanol)

$$H + RH_2 \longrightarrow H_2 + RH \qquad (2)$$

However, even when all the electrons were scavenged by acetone, a residual yield of $G_{\text{hydrogen}} = 1.05$ was obtained.[2] This exceeds the "molecular" hydrogen yield by approximately $G = 0.6$, and was attributed to the formation of H atoms by excitation processes such as

$$H_2O^* \longrightarrow H + OH \qquad (3)$$

These results are in disagreement with those obtained in the H_2O_2–O_2,[7] methanol–azide[8] and 2-propanol-azide[8] systems, where only 0.0–0.3 H atoms as such were found to react at neutral pH's.

We used bicarbonate as an electron scavenger in neutral aqueous solutions. Neutral solutions of methanol, glucose, glycerol and acetate were irradiated by 200 kV. X-rays. In all these cases, 5×10^{-2} M bicarbonate was sufficient to reduce the hydrogen yield to about 1.05, although higher yields were obtained in some cases, when no bicarbonate was used (Table I). These results confirm the recent observations of Allan, *et al.*[6] However, in all the systems studied by us a constant limiting value of $G_{\text{hydrogen}} = 1.05 \pm 0.04$ is obtained.

Similar results were obtained by using acetone as an electron scavenger.

TABLE I

HYDROGEN YIELDS FROM AQUEOUS SOLUTIONS CONTAINING BICARBONATE AND ORGANIC SOLUTES; DOSE RATE 1000 PER MINUTE

Solute	Concn. in M	G_{hydrogen}	G_{hydrogen} in the presence of 0.05M bicarbonate	Total dose
Glucose	10^{-2}	1.50	1.03	2000
Glycerol	10^{-2}	1.16	1.09	2000
Methanol	10^{-1}	1.85	1.07	2000
Acetate	10^{-1}	1.25	1.01	2000

Using formate (0.047 M) and 2-propanol (0.01 M) about 2×10^{-4} M acetone was sufficient to reduce the hydrogen yield to about 1.1. When no acetone was added, H_2 yields were much higher (about 2) at the low doses used (1000*r*).

The higher hydrogen yields obtained in the absence of an efficient electron scavenger are in agreement with previous work[9,10] and probably are due to recombination of e_{aq} or its reaction with water.

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