$$CH_3CH{=}CH_2 + KH \longrightarrow [CH_3CH_2CH_2]^-K^+ \quad (3)$$

$$[CH_3CH_2CH_2]^-K^+ + CH_3CH{=}CH_2 \longrightarrow CH_3CH_2CH_3 + [CH_2\overset{..}{-}CH\overset{..}{-}CH_2]^-K^+ \quad (4)$$

initial induction period in the reactions conducted with potassium hydride, reaction 3 proceeds more rapidly than reaction 1.

Experimental Section

Catalyst Preparation.—A mixture of 40 g of potassium metal, 352 g of heavy liquid petrolatum (Squibb's extra heavy mineral oil), and 1.0 ml of oleic acid in a 1-l. creased flask was stirred under nitrogen for 5 min at 99–100° at about 15,000 rpm, using a modified Morton stirrer. An additional 1.0 ml of oleic acid was then added and stirring was continued for 20 min before cooling to room temperature. Microscopic examination of the dispersion showed opaque, spherical particles with diameters of about 1–3 μ. Measurement of the volume of hydrogen evolved upon reacting a portion of the dispersion with 2-butoxyethanol showed that 99% of the potassium remained in the dispersion.

The potassium hydride dispersion was prepared by stirring a portion of the potassium dispersion at 190–210° in a hydrogen atmosphere for 2 hr. Microscopic examination showed that the solid was in the form of solid crystals with cross sections of 1–3 μ. Analysis as before showed that at least 89% of the potassium had been converted to the hydride.

Potassium on potassium carbonate was prepared in a nitrogen atmosphere by gradually adding pieces of the metal, washed in hexanes, to a stirred flask containing 80 g of Baker's K_2CO_3 (70% through a 200-mesh screen) at 90–120° until a total of 8 g of potassium was added. The cooled mixture was stored under heavy liquid petrolatum. Microscopic examination showed the mixture was mainly in the form of agglomerates of potassium and support, 200–400 μ in diameters, with a few smaller particles of potassium. Much of the added potassium had been lost, as analysis by alcoholysis showed that only 45% of the added potassium remained as the metal. A portion of the supported potassium in oil was converted to hydride by reacting with hydrogen as before. Microscopic examination showed that the opaque potassium had been converted to transparent crystals of approximately the original size.

Propylene Dimerization.—The catalyst and necessary additional mineral oil were charged to a 630-ml stainless steel rocking autoclave. After purging with nitrogen, the appropriate amount of Matheson CP propylene (over 99% propylene) was pressured into the autoclave. The autoclave was then heated while rocking. Reaction temperature was reached in about 45 min. The initial time was taken when a temperature of 148° was reached. When the desired pressure drop had occurred, the autoclave was cooled to room temperature without shaking. The light hydrocarbons were vented, the autoclave was opened, and dry nitrogen was bubbled through the autoclave contents at room temperature for several hours until all volatile components were removed. The catalyst slurry in mineral oil was then analyzed.

Microscopic analysis showed that both the potassium and potassium hydride dispersions had been converted to transparent spheres, 1–10 μ in diameter and light yellow to brown in color. The catalyst from potassium on potassium carbonate showed a number of transparent particles up to 250 μ in diameter and some free metal particles up to 2 mm in diameter.

Catalyst Analysis.—Portions of the used catalysts were reacted with 2-butoxyethanol in a nitogen atmosphere and the gases were collected in a gas buret. Yields were calculated from the volume change. The gaseous products were analyzed by mass spectrometry. The analysis was verified by gas–liquid partition chromatography for the samples made from the dispersions with the same results except that hydrogen was not detected.

Registry No.—Propylene, 115-07-1; potassium hydride, 7693-26-7.

Acknowledgment.—The author is indebted to Dr. S. J. Lapporte of this laboratory for suggestions concerning the mechanism of reaction.

The Reduction of Alkoxysulfonium Salts with Sodium Borohydride[1,2]

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Received May 3, 1967

In connection with our work concerning nucleophilic displacement at trigonal sulfur, we have investigated the borohydride reduction of alkoxysulfonium fluoroborates. These salts are smoothly and efficiently converted to the parent sulfides when treated with sodium borohydride in alcohols or tetrahydrofuran (THF) (Table I).

TABLE I

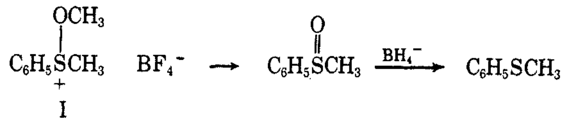
BOROHYDRIDE REDUCTION OF ALKOXYSULFONIUM SALTS

Fluoroborate	Solvent	Yield of sulfide,[a] %
Methylphenylmethoxysulfonium	Methanol	78
Phenylvinylmethoxysulfonium	Ethanol	27[b]
Diphenylmethoxysulfonium[c]	Methanol	78
Methylphenyltrideuteriomethoxysulfonium	THF	86
Dibenzylethoxysulfonium	Ethanol	90

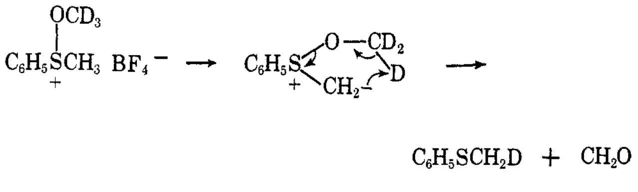
[a] Yields are for isolated and purified sulfides. [b] Phenyl vinyl sulfide. [c] The facile reduction of the diphenyl salt also provides evidence that ylides are not involved in these reactions.

Previous experiences with alkoxysulfonium salts led us to consider five possible mechanistic pathways for this reaction, employing methylphenylmethoxysulfonium fluoroborate, as illustrated in Schemes I–V. The intermediate sulfoxide depicted in Scheme I could arise through nucleophilic attack at the O-methyl by alcohol or hydride to produce an ether or methane, respectively. Scheme I was immediately ruled out by the

SCHEME I



SCHEME II



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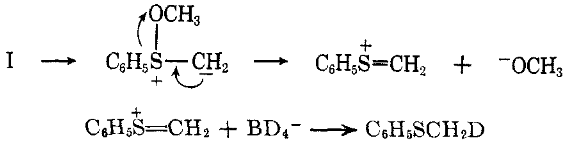

$$C_6H_5\overset{+}{S}{=}CH_2 + BD_4^- \longrightarrow C_6H_5SCH_2D$$

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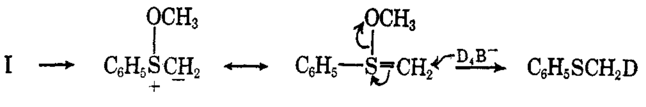
[1] (a) Part VIII in the series Chemistry of Sulfoxides; (b) Part VII: C. R. Johnson and W. G. Phillips, *J. Org. Chem.*, **32**, 1926 (1967).

[2] We gratefully acknowledge support by the National Science Foundation, Grant No. GP-5944.

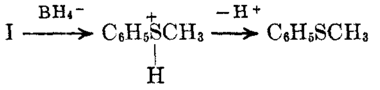
[3] Alfred P. Sloan Research Fellow, 1965–1968.

[4] National Aeronautics and Space Administration Trainee, 1965–1967.

SCHEME IV



SCHEME V



$$\mathrm{I} \xrightarrow{BH_4^-} C_6H_5\underset{\displaystyle H}{\overset{+}{S}}CH_3 \xrightarrow{-H^+} C_6H_5SCH_3$$

observation that sulfoxides are not reduced by sodium borohydride under the reaction conditions. In Schemes II, III, and IV, the borohydride first takes the role of a base, abstracting a proton from the salt to form an ylide intermediate. However, appropriate deuterium-labeling experiments indicate that none of these ylide pathways are operative.

Earlier work has shown that such ylides are readily formed and often undergo rapid collapse through the cyclic pathway shown to sulfide and a carbonyl compound.[1b] The carbonyl compound would subsequently be reduced by the borohydride (Scheme II). If such a mechanism were responsible for the production of sulfide in these reactions, methylphenyltrideuteriomethoxysulfonium fluoroborate would yield monodeuteriomethyl phenyl sulfide, provided the reaction were conducted in a nonexchanging solvent such as THF. The mass spectrum of the methyl phenyl sulfide obtained from such an experiment revealed the incorporation of only trace amounts of deuterium.

The operation of either Schemes III or IV would result in the incorporation of a deuterium in the product if sodium borodeuteride were employed. However, when I was reduced with sodium borodeuteride in methanol, the methyl phenyl sulfide produced was unlabeled. Reactions pathways analogous to Scheme III have been proposed in the reaction of certain alkoxysulfonium salts with alkoxides,[1b] in the Pummerer reaction,[5] and in methylthiomethylation reactions involving dimethyl sulfoxide and cyclohexylcarbodiimide[6] or acetic anhydride.[7] Scheme IV is adopted from the mechanism proposed for the Pummerer reaction by Oae and co-workers.[8]

The evidence forces the conclusion, although by an elimination process, that the methoxide is displaced from the sulfur by the borohydride anion. The protonated sulfide which is formed then loses a proton to form the product. This pathway is illustrated in Scheme V.

Experimental Section

General.—The alkoxysulfonium salts were prepared as previously reported.[1b] The mass spectra were determined with an Atlas CH4 mass spectrometer[9] at an ionizing potential of 70 ev and an ionizing current of 10 or 18 μa.

General Procedure for Reduction of Alkoxysulfonium Salts.—To 1 equiv of alkoxysulfonium salt in methanol, ethanol, or THF was added 4 equiv of sodium borohydride. After stirring for 30 min to 1 hr, the solvent was removed on the rotary evaporator. Ether was added to the residue and the inorganic salts which precipitated were filtered off. Removal of the ether gave the crude sulfide which was purified by distillation or recrystallization. The sulfides were identified by comparison of the melting points, mixture melting points, infrared spectra, etc., with those of authentic samples.

Deuterium-Labeling Experiments.—Methylphenylmethoxysulfonium fluoroborate was reduced with sodium borodeuteride in methanol. The mass spectrum of the methyl phenyl sulfide thus obtained exhibited a molecular ion (M) at 124 with M + 1 and M + 2 peaks of 8.66 and 5.09%, respectively, of the molecular ion intensity (calcd for C_7H_8S: M at 124 with M + 1 of intensity 8.63% and M + 2 of intensity 4.90%). Reduction of methylphenyltrideuteriomethoxysulfonium fluoroborate with sodium borohydride in THF gave methyl phenyl sulfide of mass spectrum 124, 100%; 125, 10.10%; and 126, 4.04%. Reduction of the same compound employing methanol as solvent gave sulfide of mass spectrum 124, 100%; 125, 8.65%; and 126, 4.91%.

Treatment of Methyl Phenyl Sulfoxide with Sodium Borohydride.—Methyl phenyl sulfoxide was recovered unchanged (70% recovery) when it was treated with sodium borohydride in methanol in the manner described above for alkoxysulfonium salts. The infrared spectra for the starting material and recovered product were identical.

Registry No.—Methylphenyl sulfoxide, 1193-82-4.

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[5] W. E. Parham and S. H. Groen, *J. Org. Chem.*, **30**, 728 (1965).

[6] K. E. Pfitzner and J. G. Moffatt, *J. Am. Chem. Soc.*, **87**, 5670 (1965).

[7] Sayed M. Ifzal and D. A. Wilson, *Tetrahedron Letters*, 1577 (1967); J. B. Jones and D. C. Wigfield, *ibid.*, 4103 (1965).

[8] S. Oae and M. Kise, *ibid.*, 1409 (1965), and references cited therein.

[9] The mass spectrometer was purchased from funds provided by a National Science Foundation Research Equipment Grant. We are grateful to Miss R. Van Fossen for the mass spectra.

Quaternary Benzylammonium Rearrangements with Organolithium Compounds. IV. Benzyltrimethylammonium *p*-(*t*-Butyl)phenoxide with *n*-Butyllithium[1]

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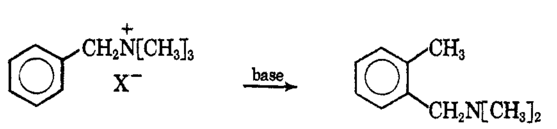
Received March 14, 1967

The conversion of benzyltrimethylammonium ion (I) to *o*,N,N-trimethylbenzylamine (II) (eq I) in 81–85% yield by the attack of the methylsulfinyl carbanion has recently been reported.[2] The simplicity of the dimethylsulfoxide system and the room-temperature conditions offer definite advantages for reaction mechanism studies over sodium amide[3] or potassium amide[4] in liquid ammonia even though the yields are slightly less than the 90–95% achieved in the latter systems. Of particular note in the methylsulfinyl case was the absence of side products which were observed when other organometallics were used in the rearrangement.[5] Therefore we wish to report on the change from high conversion to competing reactions observed with



I II (1)

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[1] (a) Supported by U. S. Public Heath Service Grant GM 13987 from the National Institute of General Medical Sciences; (b) taken in part from the M.S. thesis of T. A. B., 1967; (c) part III, A. R. Lepley and A. G. Giumanini, *J. Org. Chem.*, **32**, 1706 (1967).

[2] K. P. Klein and C. R. Hauser, *J. Org. Chem.*, **31**, 4276 (1966).

[3] S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **73**, 4122 (1951); W. R. Brasen and C. R. Hauser, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 585.

[4] W. H. Puterbaugh and C. R. Hauser, *J. Am. Chem. Soc.*, **86**, 1105 (1964).

[5] A. R. Lepley and R. H. Becker, *Tetrahedron*, **21**, 2365 (1965); *J. Org. Chem.*, **30**, 3888 (1965).