Apparently the conditions of this selective hydrogenation of 3-cyclohexene-1-carboxaldehyde to cyclohexanecarboxylaldehyde are more critical than for the similar type of hydrogenation of the myrcene-methacrolein Diels-Alder adduct to the saturated aldehyde. Kitchens[3] was able to hydrogenate this adduct to the saturated aldehyde in the presence of palladium on carbon catalyst in a rocker bomb and reported a satisfactory hydrogenation temperature range of 50–150° and a preferred temperature of 100°.

EXPERIMENTAL[4]

Hydrogenation of 3-cyclohexene-1-carboxaldehyde to cyclohexanecarboxaldehyde. Into a Parr Series 4500 1-l. medium pressure stirrer-type, electrically heated pressure reaction apparatus was placed 330 g. (3.00 moles) of 3-cyclohexene-1-carboxaldehyde (prepared by the Diels-Alder reaction of butadiene and acrolein), b.p. 54–56° (15–16 mm.), n_D^{25} 1.4691, 98.6% pure *via* gas chromatography, and 5 g. of 5% palladium on carbon catalyst (Baker and Co., Inc.). The compound was hydrogenated at a temperature of 75–80° and at 200 lb./in.^{2} of hydrogen pressure. The hydrogenation was interrupted whenever the exothermic heat of reaction carried the reaction temperature above 80° and then resumed when the heat had dissipated and the temperature was below 75°. The hydrogenation was complete in 8 hr. under these experimental conditions. The reaction time was reduced to 2.5 hr. by using a special heating mantle equipped with cooling tubes for circulation of water to dissipate the heat. The catalyst was collected on a Büchner funnel and the crude product was distilled through an 18-in. Vigreux column under reduced pressure to give 272 g. (81%) of center cut cyclohexanecarboxaldehyde, 99.0% pure (gas chromatography), b.p. 57–59° (22–24 mm.), n_D^{25} 1.4490, n_D^{20} 1.4514 (lit.[2] b.p. 62–63° (25 mm.), n_D^{20} 1.4512).

The semicarbazone of the product was recrystallized twice from ethanol-water mixtures to give fine white needles, m.p. 170–171° (lit. melting points range from 166–167°[2] to 178°[5]). The 2,4-dinitrophenylhydrazone crystallized from an ethanol–ethyl acetate mixture as bright yellow plates, m.p. 171–173° (lit.[2] m.p. 172°).

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(3) G. C. Kitchens, U. S. Patent **2,842,598** (July 8, 1958).

(4) Boiling points and melting points are uncorrected. Gas chromatography analyses were performed by E. O. Camehl of The Dow Chemical Co. Spectroscopy Service Laboratory.

(5) A. Tillotson and B. Houston, *J. Am. Chem. Soc.*, **73**, 221 (1951).

Reaction of Dimethyl Sulfoxide with Grignard Reagents

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There have been several reports of the reaction of dimethyl sulfoxide with various reagents. The reaction with thionyl chloride or acid chlorides yields chlorinated methyl sulfides,[1,2] and the reaction with acid anhydrides yields acyloxymethyl sulfide.[3,4]

Dimethyl sulfoxide is also characterized as an oxidizing agent, yielding aldehydes from some halides such as substituted benzyl bromides or higher alkyl halides,[5,6] and converting organic sulfides to the corresponding sulfoxides.[7]

The reaction of phenylmagnesium bromide and methyl *p*-tolyl sulfoxide has been reported by Potter[8] to give a tolyl benzyl sulfide in which the phenyl group from the Grignard reagent has replaced a hydrogen of the methyl group in the sulfoxide.

It is expected that the same reaction may occur with a simple sulfoxide such as dimethyl sulfoxide (DMSO). In the present work such reactions were carried out between dimethyl sulfoxide and ten Grignard reagents. Sulfides were obtained in all cases.

$$H_3CSOCH_3 + RMgX \longrightarrow H_3CSCH_2\text{—}R + Mg(OH)X$$

R = alkyl, aralkyl, and aryl group.

As described in the Experimental, when alkyl Grignard reagents (R = ethyl, *n*-propyl, and *n*-butyl) were used, considerable amounts of olefin were evolved during the reaction.

The reaction of dimethyl sulfoxide with benzylmagnesium chloride did not yield the expected methyl β-phenylethyl sulfide but methyl *o*-methylbenzyl sulfide, indicating a rearrangement.

In the case of aryl and aralkyl halides (R = phenyl, *o*-tolyl, *p*-tolyl, *p*-anisyl, *p*-bromophenyl, and β-phenylethyl), the resulting sulfides had their methylthiomethyl group in the position of the halogen of the parent halides. The reaction product from *o*-tolyl-magnesium bromide and dimethyl sulfoxide—*i.e.*, methyl *o*-methyl-benzyl sulfide was identical with the product obtained from benzylmagnesium chloride and dimethyl sulfoxide.

The yield of sulfide obtained from the reaction of dimethyl sulfoxide with Grignard reagent of *p*-dibromobenzene was low, because in anhydrous ether the conversion of this halide to the Grignard reagent was low. Therefore, this sulfide could be identified only in the form of the corresponding sulfone.

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(1) S. A. Heininger and J. Dazzi, *Chem. Eng. News*, **35**, No. 9, 87 (1957).

(2) F. G. Bordwell and B. M. Pitt, *J. Am. Chem. Soc.*, **77**, 572 (1955).

(3) W. R. Sorenson, *J. Org. Chem.*, **24**, 978 (1959).

(4) (a) L. Horner and P. Kaiser, *Ann.*, **626**, 19 (1959). (b) S. G. Smith and S. Winstein, *Tetrahedron*, **3**, 317 (1958).

(5) N. Kornblum, J. W. Powers, G. J. Anderson, W. J. Jones, H. O. Larson, O. Levand, and W. M. Weaver, *J. Am. Chem. Soc.*, **79**, 6562 (1957).

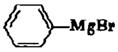
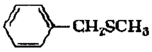
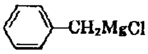
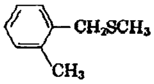
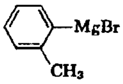
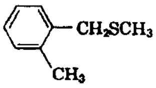
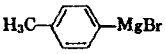
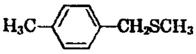
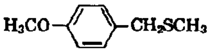
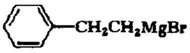
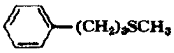
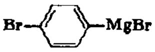
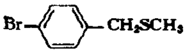
(6) I. M. Hunsberger and J. M. Tien, *Chem. & Ind.*, 88 (1959).

(7) S. Searles, Jr., and H. R. Hays, *J. Org. Chem.*, **23**, 2028 (1958).

(8) H. Potter, 137th Meeting, American Chemical Society, Cleveland, Ohio, April 5–14, 1960, p. 30.

TABLE I

REACTION OF DIMETHYL SULFOXIDE WITH GRIGNARD REAGENT

No.	Grignard Reagent	Product	Yield,[a] %	B.P./Mm.	n_D
1			31	91–92/18[b]	1.5603 (23)[b]
2			36	114–115/19[c]	1.5607 (23)[c]
3			31	122–123/27	1.5600 (25)
4			32	114–115/22	1.5480 (25)
5			21	92–93/2.0	1.5598 (23)
6			17	74–76/3.5	1.5420 (27)
7			Low[d]	—	—
8	C_3H_7MgBr	n-$C_3H_7SCH_3$	10	94–95[e]	1.4440 (20)[e]
9	n-C_4H_9MgBr	n-$C_4H_9SCH_3$	26	123–124[f]	1.4530 (16)
10	n-$C_5H_{11}MgCl$	n-$C_5H_{11}SCH_3$	30	156–157	1.4552 (16)

[a] Based on dimethyl sulfoxide. [b] Lit.[9] b.p. 120–121°/48 mm., n_D^{25} 1.5560. [c] Lit.[10] b.p. 67–68°/1.0 mm., n_D^{20} 1.5599. [d] Oxidized to corresponding sulfone. [e] Lit.[12] b.p. 94.5–95.6°, n_D^{20} 1.4436. [f] Lit.[13] b.p. 122.5°.

The results obtained are summarized in Table I. All compounds were analyzed for carbon and hydrogen.

As the substituted benzyl methyl sulfides are readily oxidized by hydrogen peroxide to the corresponding crystalline sulfones,[9,10] the latter are convenient compounds to examine in order to make certain that the positions of the substituents in the methyl aryl sulfides (No. 1–7 in Table I) were not changed from those in the parent halides. Each of the sulfones prepared in the present work showed no mixed melting point depression with the materials which were synthesized by unambiguous methods.[11]

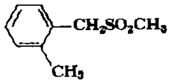
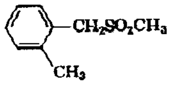
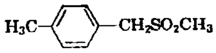
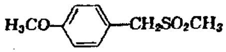
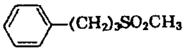
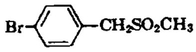
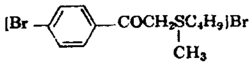
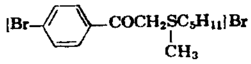
The dialkyl sulfides (9 and 10) were identified by conversion with p-bromophenacyl bromide to the corresponding sulfonium bromides.[14]

These results are given in Table II. All compounds were analyzed for carbon and hydrogen.

The mechanism of this reaction is unknown, and the roles of the hydrogen and oxygen may, at best, be speculated upon, until further data are obtained.

TABLE II

SULFONE OR SULFONIUM SALT PREPARED FROM SULFIDE

No.	Sulfone or Sulfonium Salt	Yield, %	M.P. and Mixed M.P.[a]
1		65	124–125[b]
2		66	76–77[c]
3		63	76–77[c]
4		73	131–131.5[b]
5		65	110.5–111[b]
6		45	64–65[d]
7		—	132–133[b]
9		23	101–102[d]
10		30	98–99[d]

[a] All melting points are uncorrected. [b] Recrystallization from aqueous methanol. [c] Recrystallization from benzene-hexane. [d] From ether.

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

(10) C. R. Hauser, S. W. Kantor, and W. R. Brasen, *J. Am. Chem. Soc.*, **75**, 2660 (1953).

(11) G. G. Urquhart, J. W. Gates, Jr., and R. Conner, *Org. Syntheses*, Coll. Vol. III, 363 (1955).

(12) C. C. Price and R. G. Gillis, *J. Am. Chem. Soc.*, **75**, 4750 (1953).

(13) L. Bateman and J. I. Cunneen, *J. Chem. Soc.*, 1596 (1955).

(14) M. Jurecek, M. Vecera and J. Gasparic, *Chem. Listy*, **48**, 582 (1954); *Chem. Abstr.*, **48**, 8129 (1954).

EXPERIMENTAL

Preparation of Grignard reagents. The Grignard reagents were prepared in the usual manner by the reaction of 0.5 mole of organic halides with 12.5 g. of magnesium turnings in anhydrous ether. After the addition of the halides, the solution was refluxed for 2 hr.

Formation of sulfides. To a vigorously stirred and cooled (below 10°) Grignard solution was added, over a period of 1 hr., 27.3 g. (0.35 mole, No. 1–5) or 31.2 g. (0.40 mole, No. 6–10) of dimethyl sulfoxide dissolved in about equal quantity of anhydrous ether. A grey-white solid deposition began almost immediately and in some cases continued stirring was impossible. The reaction mixture was then heated at the reflux point for an additional 3 hr. and allowed to stand overnight at room temperature.

When the temperature of the reaction mixture of dimethyl sulfoxide with alkyl Grignard reagent (R = ethyl, *n*-propyl, and *n*-butyl) had risen nearly to room temperature, a fairly vigorous evolvement of gas was observed. After passing the gas through a large excess of bromine, the bromine was removed and the residual oil was purified as usual. From gas chromatographic and infrared spectral data, in the case of *n*-propylmagnesium bromide, the oily product was identical with 1,2-dibromopropane. In the other two cases, the 1,2-dibromo derivative of the olefin which corresponded to the parent alkyl halide was obtained.

After adding 500–800 ml. of ice water containing about 50–80 ml. of concd. hydrochloric acid, the ether layer was separated, washed twice with water, and dried over anhydrous sodium sulfate. The solvent was removed and the residue distilled *in vacuo* to yield the strongly smelling sulfide.

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Reaction of Methyl Bromide with Dimethylformamide

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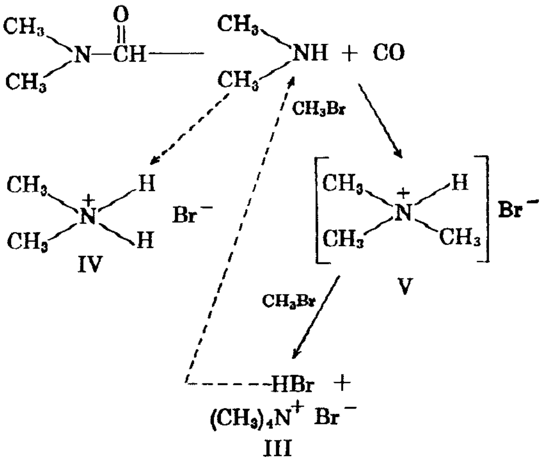
In attempts to quaternize the diamines, *N*-(5-dimethylamino-2-pentynyl)-8-methoxy-1,2,-3,4-tetrahydroquinoline (I) and *N*-(4-dimethylamino-2-butynyl)-1,2,3,4-tetrahydroquinoline (II), the use of *N,N*-dimethylformamide (DMF) as the solvent appeared to be practicable; it was found by other investigators[1] that amines which resisted quaternization in other solvent systems often underwent facile quaternization in *N,N*-dimethylformamide. Treatment of I or II with an excess of methyl bromide in *N,N*-dimethylformamide in a sealed tube at 80° for twenty-four hours resulted in the separation of a white crystalline powder which after washing with hot isopropyl alcohol showed an elemental analysis corresponding to tetramethylammonium bromide (III). In an attempt to rationalize the formation of III, a mixture of methyl bromide and *N,N*-dimethylformamide was heated in a sealed tube for six days; the tube was opened and the white crystalline product was collected. This solid was found to consist of two compounds which after recrystallization were identified as tetramethylammonium bromide and dimethylammonium bromide (IV).

It is proposed that the two products were formed by decomposition of *N,N*-dimethylformamide into dimethylamine and carbon monoxide, and that the amines thus formed were quaternized by the methyl bromide as follows:



The evolution of carbon monoxide was confirmed by a positive reaction with phosphomolybdic acid–palladium chloride reagent solution.[2]

The identity of products III and IV was confirmed by comparison of their infrared spectra and melting points with those of known samples of the compounds. In subsequent experiments the molar ratio of *N,N*-dimethylformamide to methyl bromide was varied to study the effect on the yields of products. Maximum yields of 37% of IV (based on methyl bromide) were obtained when a molar ratio of eight parts of *N,N*-dimethylformamide to one part of methyl bromide was used. A negligible amount of IV was obtained when two parts of *N,N*-dimethylformamide and one part of methyl bromide were combined. It was of interest that no trimethylammonium bromide (V) could be isolated from any reaction mixture.

EXPERIMENTAL

Dimethylformamide (Eastman White Label) purified by distillation from calcium hydride and contained in a 25-ml. Carey tube was cooled to $-70°$ in a Dry Ice–acetone bath and the required amount of methyl bromide was added. The tube was then sealed and was placed in a heating jacket maintained at 80° for 6 days. The tube was cooled

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[1] C. K. Bradsher and H. Berger, *J. Am. Chem. Soc.*, 80, 930 (1958).

[2] F. Feigl, *Spot Tests in Organic Analysis*, Elsevier Publishing Co., New York, 1956, p. 327.