values calculated from known bond moments and ring conformations.

A dipole moment of 1.87 D. has been reported[13] for tetrahydrothiophene. If one takes the CSC angle in this compound as 100°, the observed moment can be considered as the vector sum of two CS bond moments of 0.935/cos 50°, or 1.46 D.

Bond angles and bond lengths in 1,2-dithiolane-4-carboxylic acid have been determined by Foss and Tjomsland[21] based on X-ray diffraction studies. Based upon their data, the average angle between the valence bonds of each sulfur atom is 94.6° and the value of the dihedral angle between the CSS plane and the SSC plane is 26.6°. Then, by assuming the angular conformation of the 1,2-dithiolane ring in 2,3-dithiaspiro[4.5]decane to be the same as in the corresponding carboxylic acid, neglecting any small contribution of the cyclohexane ring, and taking 1.46 D. as the C–S bond moment, the calculated moment of 2,3-dithiaspiro[4.5]decane is 2.82 D., in good agreement with the observed moment of 2.85 D.

The moments of the selenium-containing compounds cannot be treated so precisely because of lack of information about the C–Se–Se bond angles. However, monoselenides usually have moments only slightly smaller than monosulfides,[22] and it is, therefore, not unexpected to find that the dithiolanes and diselenolanes have similar moments or that the moment of the thiaselenenates, in the absence of a significant degree of polarization, is again similar to those of its isologs.

Turning now to the carboxylic acids, 1,2-dithiolane-4-carboxylic acid (I) can be treated as containing a planar ring with a moment of 2.85 D. The contribution of the carboxyl group in I is taken from the observed moment of cyclopentanecarboxylic acid (1.70 D.) and the angle of the C–COOH bond to the plane of the ring is assumed to be one-half the normal tetrahedral angle of 110°. The angle of the carboxyl moment to the C–COOH bond is taken as 74°.[23]

Hydrogen bonding of the carboxylic hydrogen to the disulfide bond would restrict rotation of the carboxyl group and result in a molecule with conformation Ia, having a calculated dipole moment of 1.4 D. Conversely, conformation Ib, resulting from interaction of the S–S bond with the carbonyl oxygen, would produce a moment of 4.1 D. The moments observed for the free acids as well as for the methyl ester of 1,2-dithiolane-4-carboxylic acid are in surprisingly good agreement with the moment calculated assuming unrestricted rotation of the carboxyl group, 3.1 D. This further substantiates the contention that little, if any, interaction occurs between the carboxyl group and the disulfide bond.

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(21) O. Foss and O. Tjomsland, *Acta Chem. Scand.*, **12**, 1810 (1958).

(22) For example, the moment of diphenyl sulfide is quoted as 1.5 D., that of diphenyl selenide 1.4 D.: R. J. W. Le Fèvre, "Dipole Moments," Methuen and Co., Ltd., London, 1963, pp 134,135.

(23) C. P. Smyth, ref 12, p 308.

Sulfoxide–Carbodiimide Reactions. III.[1] Mechanism of the Oxidation Reaction

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Contribution No. 36 from the Syntex Institute of Molecular Biology, Stanford Industrial Park, Palo Alto, California.

Received December 23, 1965

Abstract: The mechanism of the oxidation reaction resulting from treatment of an alcohol with dimethyl sulfoxide and dicyclohexylcarbodiimide in the presence of a proton source has been elucidated through isotope experiments. Hydrolysis of dimethylsulfur dibromide with ^{18}O-water gave ^{18}O-dimethyl sulfoxide which was used for the oxidation of *p*-nitrobenzyl alcohol. The resulting *p*-nitrobenzaldehyde contained no isotope but the concomitantly formed dicyclohexylurea was labeled to the same extent as the starting sulfoxide. This confirms the initial formation of a sulfoxide–carbodiimide adduct (I) which can be attacked by the alcohol to give the alkoxysulfonium salt (II). Oxidation of 1,1-dideuteriobutanol led to 1-deuteriobutyraldehyde and monodeuteriodimethyl sulfide which were isolated by gas–liquid chromatography. Isolation of the latter compound confirms that proton abstraction from the alkoxy group of II is brought about *via* a cyclic mechanism involving a sulfur ylid. The same conclusion can be drawn from oxidation of butanol in hexadeuteriodimethyl sulfoxide which gives pentadeuteriodimethyl sulfide and butyraldehyde.

In earlier papers of this series[1,3] we have described the development of an efficient and extremely mild method for the oxidation of alcohols to the corresponding aldehydes or ketones. This method involves the reaction at room temperature of the alcohol with dimethyl sulfoxide (DMSO) and dicyclohexylcarbodiimide (DCC) in the presence of a proton source such as anhydrous phosphoric acid or pyridinium trifluoroacetate. The reaction has recently been applied with considerable success by a number of workers.[4]

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(1) Part II is K. E. Pfitzner and J. G. Moffatt, *J. Am. Chem. Soc.*, **87**, 5670 (1965).

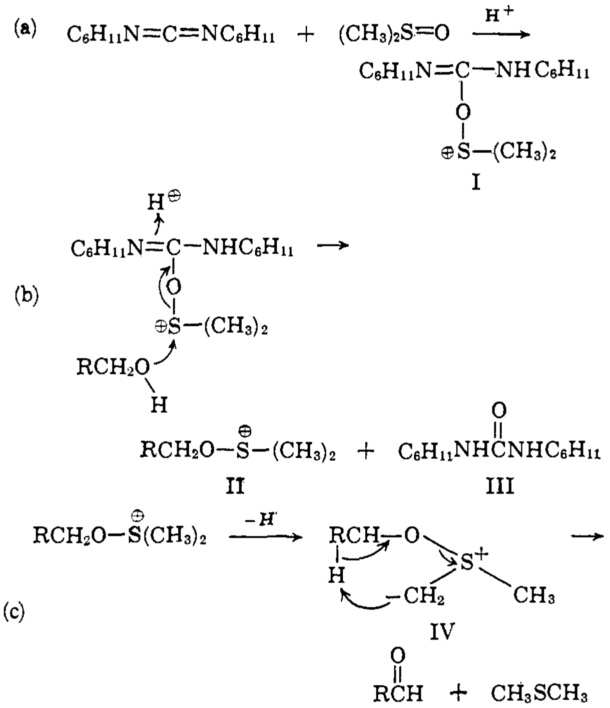
(2) Syntex Postdoctoral Fellow, 1964–1965.

(3) (a) K. E. Pfitzner and J. G. Moffatt, *J. Am. Chem. Soc.*, **85**, 3027 (1963); (b) K. E. Pfitzner and J. G. Moffatt, *ibid.*, **87**, 5661 (1965).

(4) For examples see (a) B. R. Baker and D. H. Buss, *J. Org. Chem.*, 30, 2304, 2308 (1965); (b) G. Buchi, D. L. Coffen, K. Kocsis, P. E. Sonnet, and F. E. Zeigler, *J. Am. Chem. Soc.*, **87**, 2073 (1965); (c) J. D. Albright and L. Goldman, *J. Org. Chem.*, 30, 1107 (1965); (d) J. R. Dyer, W. E. McGonigal, and K. C. Rice, *J. Am. Chem. Soc.*, **87**, 654 (1965).

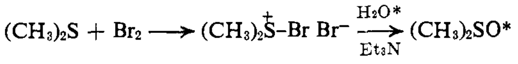
We have already proposed a mechanism for this reaction as outlined in Scheme I[3b] and in this paper we present the results of isotope experiments that convincingly confirm these predictions.

Scheme I



The intermediacy of the alkoxysulfonium salt II mechanistically relates this reaction to the oxidation of various reactive alkyl halides or tosylates to carbonyl compounds upon heating with DMSO.[5] Oxidations have also recently been described in which intermediates of type II are formed by reactions of DMSO with alkyl chloroformates[6] or with alcohols in the presence of acid anhydrides.[7]

Our first objective was to confirm the initial formation of the DMSO–DCC adduct through the use of ^{18}O-labeled DMSO. The latter compound has been prepared through hydrolysis of dimethylmethoxysulfonium perchlorate with ^{18}O-water,[8] but we have used a different route. The reaction of dimethyl sulfide with bromine in carbon tetrachloride led to an almost quantitative yield of crystalline dimethylsulfur dibromide (V).[9] The hydrolysis of dialkylsulfur dihalides to the corresponding sulfoxides has been described in the early literature.[10] We have examined the hydrolysis of V to dimethyl sulfoxide under a variety of conditions, following the reactions by gas–liquid chromatography. In terms of efficient use of the water employed, optimal results were obtained on reaction of 2 equiv of V with 1 equiv of water and 4 equiv of triethylamine in tetrahydrofuran. The product isolated by preparative gas–liquid chromatography from such a reaction was indistinguishable from authentic DMSO by infrared and nuclear magnetic resonance spectroscopy. These contions were then applied using a sample of ^{18}O-labeled water which was obtained from the Weizmann Institute of Science, Rehovoth, Israel. Following removal of the precipitated triethylamine hydrobromide, crude ^{18}O-DMSO was isolated by distillation. As obtained it was contaminated by two other substances and purification was achieved by preparative gas–liquid chromatography.



$$(CH_3)_2S + Br_2 \longrightarrow (CH_3)_2\overset{+}{S}\text{-}Br\ Br^- \xrightarrow[Et_3N]{H_2O^*} (CH_3)_2SO^*$$

V

The ^{18}O content of the purified product was determined by direct mass spectrometric analysis. The most unambiguous results came from comparison of the molecular ions corresponding to the ^{16}O (*m/e* 78, relative abundance 55%) and ^{18}O (*m/e* 80, relative abundance 13.5%) species in the purified mixture. After correction of the *m/e* 80 peak for 4.2% natural abundance of ^{34}S and for a small peak (5.5% of the intensity of *m/e* 78) at *m/e* 80 in the spectrum of unlabeled DMSO, the sample was found to contain 15.0% ^{18}O. Confirmation of this figure came for a similar comparison of the peaks at *m/e* 48 (presumably SO$^+$, relative abundance 14%) and *m/e* 50 (relative abundance 3%) which indicated 14.5% ^{18}O excess.[11] Calculations based upon the base peak at *m/e* 63 (100% relative abundance) are less reliable due to the presence of a substantial fragment at *m/e* 65 in unlabeled DMSO. More precise measurements of isotope content could have been obtained by prior combustion and oxidation of the samples to carbon dioxide[8] but the requisite equipment was not readily available.

The ^{18}O-DMSO obtained above was then used together with dicyclohexylcarbodiimide and anhydrous orthophosphoric acid for the oxidation of *p*-nitrobenzyl alcohol to *p*-nitrobenzaldehyde, as previously described.[1] The dicyclohexylurea that separated during the reaction was separated and recrystallized from methanol. Following removal of excess DCC by addition of oxalic acid, the resulting *p*-nitrobenzaldehyde was purified by sublimation and shown to be pure by thin layer chromatography. Mass spectrometric analysis of the various products clearly showed that the oxygen from DMSO was ultimately located in the dicyclohexylurea. Thus, the spectrum of the crystalline aldehyde showed a base peak (100%) at *m/e* 150 (M − 1) and a molecular ion (88% relative abundance) at *m/e* 151. A small peak (9% relative abundance) at *m/e* 152 can be almost entirely accounted for by the natural abundance of ^{13}C and ^{15}N, and no detectable peak occurred at *m/e* 153. These, and all other, features of the spectrum were identical with those from an authentic nonisotopically enriched sample and indicate that the aldehyde oxygen does *not* originate from the DMSO. This point has been further corroborated by the recent report[7a] that oxidation of several ^{18}O-labeled alcohols by the DMSO–DCC method led to aldehydes with retention of the isotope. Both experi-

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(5) (a) 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); (b) N. Kornblum, W. J. Jones, and G. J. Anderson, *ibid.*, **81**, 4113 (1959); (c) I. M. Hunsberger and J. M. Tien, *Chem. Ind.* (London), 88 (1959), and other references cited in ref 3b.

(6) D. H. R. Barton, B. J. Garner, and R. H. Wightman, *J. Chem. Soc.*, 1855 (1964).

(7) (a) J. D. Albright and L. Goldman, *J. Am. Chem. Soc.*, **87**, 4215 (1965); (b) K. Onodera, S. Hirano, and N. Kashimura, *ibid.*, **87**, 4652 (1965).

(8) N. J. Leonard and C. R. Johnson, *ibid.*, **84**, 3701 (1962).

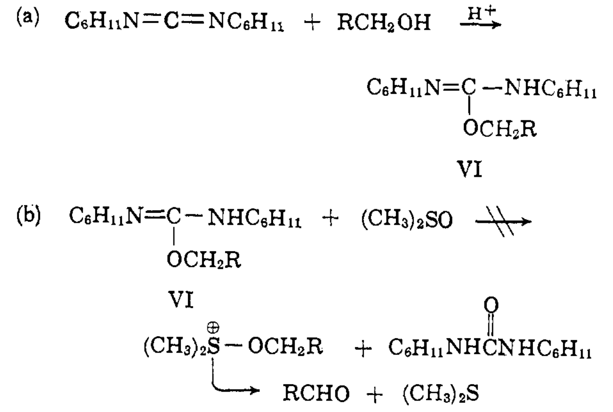
(9) (a) A. Hantzsch and H. Hibbert, *Ber. Deut. Chem. Ges.*, 40, 1508 (1907); (b) P. Haas, *Biochem. J.*, **29**, 1297 (1935).

(10) (a) For key references see E. E. Reid in "Organic Chemistry of Bivalent Sulfur," Vol. II, Chemical Publishing Co., New York, N. Y., 1960, p 49; (b) E. Fromm, *Z. Angew. Chem.*, **24**, 1125 (1911).

(11) These figures have been rounded to the nearest 0.5% since this is the limit of accuracy in measuring the relative abundancies.

ments clearly rule out the intermediacy of pseudoureas (*e.g.*, Scheme II), a conclusion that we had previously drawn[3b] from the inertness of preformed 1,3-dicyclohexyl-2-*p*-nitrobenzylpseudourea (VI, R = *p*-nitrophenyl) under the conditions of the oxidation reaction.

Scheme II



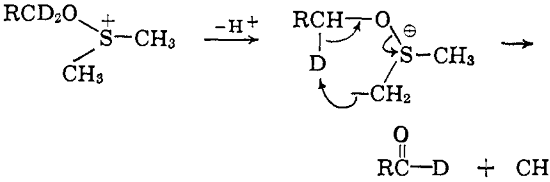
Examination of the mass spectrum of the recrystallized dicyclohexylurea (III) that had separated during the oxidation reaction using ^{18}O-DMSO clearly indicated the presence of substantial amounts of isotope. Both the molecular ion (*m*/*e* 224, relative intensity 23%) and the fragment with *m*/*e* 143 ($C_6H_{11}NHCONH_3^+$ 14%) were associated with smaller peaks at *m*/*e* 226 and 145, respectively, that were not present in the spectrum of unlabeled III.[12] The magnitude of these peaks both indicated the presence of 14.5% ^{18}O. The other major peaks in the spectrum (*m*/*e* 56, relative intensity 100%, and *m*/*e* 99, relative intensity 28%) do not appear to contain oxygen and show no satellite peaks heavier by 2 mass units.

The above experiment thus unequivocally demonstrates the quantitative transfer of the oxygen from DMSO into the ultimately isolated dicyclohexylurea and confirms the initial formation of the adduct I from DMSO and DCC. A closely related acid-catalyzed addition of DMSO to ketenes and ketenimines has recently been proposed by Lillien.[13]

The second step in the proposed mechanism (Scheme I, step b) involves nucleophilic attack by an alcohol molecule upon the sulfoniumisourea derivative I with formation of the alkoxysulfonium compound II and highly insoluble dicyclohexylurea (III). Such an attack finds analogy in the known hydrolysis[8,14,15] and alcoholysis[16,17] of alkoxysulfonium salts which are known to occur by S$_N$2 displacement.

The final step in the proposed mechanism requires abstraction of a proton from the α-carbon of the alkoxy group in II and concerted collapse of the resulting intermediate to the carbonyl compound and dimethyl sulfide. Since the oxidation is carried out in the presence of free acid phosphoric acid or pyridinium trifluoroacetate (usually using 2 equiv of pyridine/equiv of acid) the true bimolecular abstraction of such a proton is difficult to accept. On the other hand, it is well known that the protons of methyl groups directly attached to positively charged sulfur undergo ready exchange with D_2O[18] and the rate of this exchange is enhanced by several powers of ten in alkoxysulfonium derivatives such as II.[14] Hence, under the neutral or slightly acidic reaction conditions, it is most reasonable to conclude that proton abstraction promoted by either pyridine or the second dissociation of phosphoric acid[19] will lead to the sulfur d-orbital stabilized[20] ylid IV. The carbanion of IV can then act as an internal base and IV can collapse *via* a cyclic mechanism as in Scheme I (c) to the carbonyl compound and dimethyl sulfide.

We have confirmed the intramolecular proton abstraction above by two routes using deuterium-labeled substrates. Firstly, 1,1-dideuteriobutanol-1[21] was oxidized in the presence of unlabeled DMSO, DCC, and anhydrous phosphoric acid. Following removal of dicyclohexylurea the crude reaction mixture was directly separated by preparative gas-liquid chromatography, giving homogeneous samples of butyraldehyde and dimethyl sulfide. The mass spectrum of the dimethyl sulfide showed the molecular ion to be at *m*/*e* 63 (relative intensity 100%) corresponding to the monodeuterio species $[CH_3SCH_2D]^+$. The peak at *m*/*e* 62, which could represent either the nondeuterated molecular ion $[CH_3SCH_3]^+$ or an M − 1 fragment from the monodeuterio species, had a relative abundance of only 41%. The other intense peaks in the spectrum were at *m*/*e* 47 (CH_3S^+, relative intensity 100%) and *m*/*e* 48 (CDH_2S^+, relative intensity 66%). These data conclusively demonstrate the intramolecular proton abstraction step as follows.



In addition, the nuclear magnetic resonance spectrum of the purified butyraldehyde clearly confirmed the presence of only deuterium directly attached to the carbonyl group. Thus, the aldehydic proton present as a triplet (J = 1.9 cps) centered at 586.5 cps in unlabeled butyraldehyde was completely absent. Also the C_2-methylene group appeared as a clean triplet at 138, 144.5, and 151 cps whereas in unlabeled butyraldehyde each of these peaks was further split into a doublet (J = 1.9 cps) by the aldehydic proton. All other features of the spectra were superimposable.

A somewhat analogous experiment was also done in which unlabeled 1-butanol was oxidized by hexadeuteriodimethyl sulfoxide in the presence of DCC and anhydrous phosphoric acid. Once again the resulting

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[12] The spectrum of nonenriched dicyclohexylurea actually showed a small peak at *m*/*e* 226 which was 2% as intense as the molecular ion at *m*/*e* 224. The origin of this peak remains obscure and the calculated ^{18}O content of our enriched sample has been corrected for its presence.

[13] I. Lillien, *J. Org. Chem.*, **29**, 1631 (1964).

[14] S. G. Smith and S. Winstein, *Tetrahedron*, **3**, 317 (1958).

[15] C. R. Johnson, *J. Am. Chem. Soc.*, **85**, 1020 (1963).

[16] S. G. Smith, Ph.D. Thesis, University of California at Los Angeles, 1959, cited ref 8.

[17] C. R. Johnson and W. G. Phillips, *Tetrahedron Letters*, 2101 (1965).

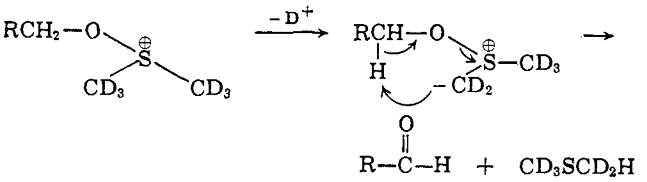
[18] W. von E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, **77**, 521 (1955).

[19] It has previously been pointed out[3b] that the oxidation reaction fails, or is extremely slow, in the presence of phosphoric acid diesters or other strong acids.

[20] G. Cilento, *Chem. Rev.*, **60**, 147 (1960).

[21] A generous gift of Dr. C. Fenselau of the Department of Chemistry, Stanford University.

butyraldehyde and dimethyl sulfide were isolated by preparative gas–liquid chromatography. As would be expected the aldehyde was free of isotope. The mass spectrum of the dimethyl sulfide, however, showed its most intense peak at *m/e* 67 corresponding to the molecular ion $[CD_3SCD_2H]^{+\cdot}$. Only a low-intensity peak (relative intensity 11%) was present at *m/e* 68. The two other intense peaks in the spectrum were at *m/e* 49 and *m/e* 50 (relative intensities 79 and 81%) and correspond to the fragments CD_2HS^+ and CD_3S^+, respectively. There is thus almost equal probability of fragmentation on either side of the sulfur atom.



These various experiments taken together quite unambiguously confirm the mechanism of the oxidation reaction as originally proposed[3b] and outlined in Scheme I. A number of further studies based upon reactions of the key intermediate I have been carried out in this laboratory and will be reported in subsequent papers in this series.

Experimental Section

General Methods. Thin layer chromatography was conducted on 0.25-mm layers of silica gel GF from Brinkmann Instruments, Inc. Spots were visualized by their ultraviolet absorption or by spraying with 5% ammonium molybdate in 10% sulfuric acid followed by heating in a 150° oven. Nuclear magnetic resonance spectra were determined by Mr. John Murphy on a Varian A-60 instrument using solutions in deuteriochloroform and are measured in cycles per second downfield from a standard of tetramethylsilane. Gas–liquid chromatography was done using a Wilkens Aerograph Model 90-P2 instrument. We are extremely grateful to Dr. Boris Weinstein of Stanford University for permission to use this instrument. Mass spectra were obtained with the cooperation of Dr. A. Duffield of Stanford University and Dr. A. L. Burlingame of the University of California, Berkeley, using either a CEC Model 21-103C spectrometer with a 200° heated inlet system and an ionizing voltage of 70 ev, or an Atlas CH-4 spectrometer with a direct inlet system and an ionizing voltage of 70 ev.

Dimethylsulfur Dibromide (V). Bromine (1.8 ml, 33 mmoles) was added dropwise over 40 min to a vigorously stirred, ice-cooled solution of dimethyl sulfide (2.43 ml, 33 mmoles) in carbon tetrachloride (30 ml). The resulting yellowish orange crystals were removed by filtration and washed with cold carbon tetrachloride. After drying *in vacuo*, 6.8 g (92%) of dimethylsulfur dibromide was obtained. Recrystallization from carbon tetrachloride gave V as yellow needles, mp 90–91° (Hass[9b] reports mp 93–94°). The nmr spectrum in deuteriochloroform showed only a singlet at 158 cps (*cf.* a singlet at 156 cps for DMSO).

Dimethyl Sulfoxide-^{18}O. Solid dimethylsulfur dibromide (5.0 g, 22.5 mmoles) was added portionwise over 15 min to a vigorously stirred solution of triethylamine (6.3 ml, 45 mmoles, freshly distilled from potassium hydroxide) and ^{18}O-labeled water (0.20 ml, 11 mmoles, diluted to contain approximately 15% ^{18}O) in 15 ml of tetrahydrofuran (freshly distilled from lithium aluminum hydride). The temperature of the reaction was maintained below 50° by occasional cooling in ice. The precipitate of triethylamine hydrobromide was removed by centrifugation and washed twice with ether. The combined yellow supernatant and washings were distilled at room temperature (15 mm) to remove the solvent and the tan residue was distilled in a short-path apparatus (60–70° at 0.3 mm) giving 1.03 g of a pale yellow liquid. Purification of this material was effected by preparative gas–liquid chromatography on a 20 ft × $^3/_8$ in. column of SE-30 on 45–60 Chromosorb P[22] using a column temperature of 135° and a helium flow rate of 120 ml/min. This gave ^{18}O-DMSO (430 mg, 45%, analytical retention time 8.1 min) contaminated with traces of faster and slower compounds (6.4 and 8.6 min, respectively). Rechromatography on a 0.25 in × 2 m column of 20% Carbowax 20 M on hexamethyldisilazane treated 60–80 Chromosorb P maintained at 155° and with a helium flow of 85 ml/min gave pure DMSO giving a single peak by analytical gas–liquid chromatography. Mass spectrometry of this material on the CEC Model 21-103 C spectrometer (see text) indicated an ^{18}O content of 14.5–15.0%.

Oxidation of *p*-Nitrobenzyl Alcohol with ^{18}O-DMSO. Recrystallized *p*-nitrobenzyl alcohol (25 mg, 0.16 mmole) was dissolved in ^{18}O-DMSO (0.055 ml, 0.75 mmole) and anhydrous benzene (0.10 ml) containing DCC (91 mg, 0.44 mmole). A solution of anhydrous orthophosphoric acid in ether (10 μl of 5 *M*, 0.05 mmole) was added and after 12 hr at room temperature the crystalline dicyclohexylurea was removed by filtration and washed with benzene. This material (50 mg) was recrystallized from methanol and had mp 232–234°. A saturated methanolic solution of oxalic acid (40 mg) was then added to the filtrate and after 30 min the precipitated dicyclohexylurea was removed by filtration. The filtrates were extracted with 5% sodium bicarbonate and then twice with water, dried over magnesium sulfate, and evaporated to dryness, leaving 32 mg of crystalline residue. Thin layer chromatography of this product (chloroform–ethyl acetate, 4:1) showed it to contain 90–95% *p*-nitrobenzaldehyde and 5–10% *p*-nitrobenzyl alcohol.[23] Sublimation at 90° (0.2 mm) gave the crystalline aldehyde (21 mg, mp 98°) contaminated only by a trace of dicyclohexylurea (infrared band at 3325 cm^{-1}). Resublimation gave the pure aldehyde indistinguishable from an authentic sample. Mass spectrometry (CEC, heated inlet, 70 ev) showed the compound to contain no ^{18}O (see text). Mass spectrometry (Atlas CH-4, direct inlet system, 70 ev) of the recrystallized dicyclohexylurea (see text) indicated the presence of 14.5% ^{18}O.

Oxidation of 1,1-Dideuteriobutanol. A solution of anhydrous orthophosphoric acid in ether (0.02 ml of 5 *M*, 0.1 mmole) was added to a solution of 1,1-dideuteriobutanol[21] (1.1 mmoles) and DCC (548 mg, 2.65 mmoles) in DMSO (0.3 ml). After 15 hr at room temperature the dicyclohexylurea was removed by centrifugation and the total reaction mixture was directly chromatographed in three portions on a 0.25 in. × 2 m column of 20% Carbowax 20 M on hexamethyldisilazane treated Chromosorb P[22] maintained at a temperature of 35–40° and with a helium flow rate of 30 ml/min. The first three peaks, identified as ether, dimethyl sulfide, and butyraldehyde by comparison with standards, were well resolved and were collected in liquid nitrogen traps. The mass spectrum of the dimethyl sulfide peak (CEC spectrometer) showed its most intense peak at *m/e* 63 corresponding to monodeuteriodimethyl sulfide (see text). The nmr spectrum of the purified aldehyde clearly demonstrated it to be 1-deuteriobutyraldehyde as described in the text.

Oxidation of Butanol with Hexadeuteriodimethyl Sulfoxide. 1-Butanol (0.20 ml, 2.2 mmoles) and DCC (1.0 g, 4.8 mmoles) were dissolved in anhydrous 99% hexadeuteriodimethyl sulfoxide (0.50 ml, 6 mmoles). Following addition of a solution of anhydrous orthophosphoric acid in ether (0.025 ml of 3.4 *M*, 0.85 mmole) the mixture was kept at room temperature for 8 hr. The resulting crystalline dicyclohexylurea was removed by centrifugation and the supernatant was directly separated by gas–liquid chromatography on a column identical with that described above in the experiment with 1,1-dideuteriobutanol. The dimethyl sulfide and butyraldehyde were cleanly separated and collected in liquid nitrogen traps. The mass spectrum (CEC spectrometer) of the dimethyl sulfide had its most intense peak at *m/e* 67 corresponding to the molecular ion $[CD_3SCD_2H]^+$.

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[22] Wilkens Instrument and Research, Inc., Walnut Creek, Calif.

[23] The residual alcohol is probably due to the low molar ratio of DMSO used in this experiment. Using a large excess of DMSO the yield is quantitative.[3b]