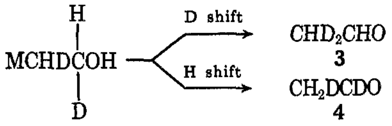
Thus, as shown in eq 7 [M = Pd(II) or Tl(III)], either mode of hydroxymetalation will give a choice of

$$M + C_2H_2D_2 \xrightarrow{H_2O}$$



$$\mathrm{MCHDC(H)(D)OH} \begin{cases} \xrightarrow{\text{D shift}} \mathrm{CHD_2CHO} \; \mathbf{3} \\ \xrightarrow{\text{H shift}} \mathrm{CH_2DCDO} \; \mathbf{4} \end{cases} \qquad (7)$$

an H or a D transfer. The ratio of the tendencies for H to transfer as opposed to D is a measure of the isotope effect. Thus the **4**/**3** ratio measures the isotope effect. The value found for Pd(II) was 1.70 and that for Tl(III) was 1.92. These isotope effects, in conjunction with the kinetic isotope effects, support the earlier conclusion[7,9] that hydroxymetalation is the rate-determining step in both oxidations.

The magnitude of the isotope effects is not large in either oxidation, suggesting that both bond breaking and bond making are important in the transition state.

Experimental Section

Reagents.—The preparation and analysis of the $Tl(ClO_4)_3$[9] and palladium(II) chloride[7] stock solutions have been described. The C_2D_4 was purchased from Volk Radiochemical Co., and the D_2O from Bio-Rad Laboratories.

Preparation of *cis*- and *trans*-Ethylene-d_2.—The procedures were essentially the same as that used previously for preparing *cis*- and *trans*-ethylene-d_2 from acetylene-d_2.[16] However, in the present work undeuterated acetylene was reduced in D_2O. The reactions were carried out in a 750-ml soft-drink bottle capped with a metal cap having holes sealed by a rubber liner. The bottle could be evacuated or pressured with gas by means of syringe needles inserted through the rubber liner. An excess of the reducing solution (chromous chloride for the trans isomer and copper activated zinc for the cis[16]) in about 150 ml of D_2O was prepared in the bottle and the bottle was evacuated. The bottle was then pressured to about 5 psig with acetylene and agitated on a mechanical shaker for several hours. Samples were removed by means of a syringe equipped with needle and analyzed by infrared and mass spectrometry. All the acetylene had reacted and each isomer could be shown to be uncontaminated by the other isomer by means of the infrared spectra.[16]

Oxidation Rates.—These reactions were carried out in tubes which were capped in the same fashion as the pop bottles. The volume of the tube is about 17 ml. Five milliliters of a Pd(II) or Tl(III) solution which was about 0.1 *M* in the metal ion and 0.5 *M* in $HClO_4$ was put in the tube, the tube was capped and evacuated, and the ethylene-d_4 or ethylene-d_2 was admitted to the tube. The tubes were agitated for periods from 1 to 10 min and then a gas sample was removed by means of a syringe for infrared. The tube was then opened, zinc dust was added to reduce any unreacted metal ion, and the perchloric acid was neutralized with sodium acetate. About 1 ml of solution was then injected into a gas chromotograph and the acetaldehyde peak was collected in a 100% collection tube and analyzed by mass spectrometry. This technique has been described.[17] A 6-ft Carbowax 20M on ABS (70–80 mesh) column at 80° was used for the collection.

In the case of the ethylene-d_4 the deuterium content was obtained by the relative intensities of the parent ions.[18] It was found that the quantities of lower deuterated acetaldehydes, such as acetaldehyde-d_3, increased with time; so the runs were carried to small conversions. Reaction times were 2 min or less. For both Tl(III) and Pd(II) the acetaldehyde-d_4 content was between 95 and 98% for triplicate runs with the remainder being mainly acetaldehyde-d_3.

The ethylene-d_2 runs were carried out in the same fashion. The deuterium distributions were determined by the ratio of the *m/e* 30 (CDO) and 29 (CHO) peaks. Previous work indicates[18] that this should be a good measure of CD_2HCHO and CH_2DCDO contents.

Preliminary work indicated that *cis*- and *trans*-dideuteroethylenes both gave the same ratios of **3** and **4**. Because of ease of preparation the trans isomer was used for the final quantitative work. The $C_2H_2D_2O$ originally formed exchanged with solvent to give lower deuterated acetaldehydes. For that reason short reaction times were employed. Two runs with 0.28 *M* $Tl(ClO_4)_3$ in 2 *M* $HClO_4$ at reaction times of less than 10 min gave identical **4**/**3** ratios of 1.92. The formation of lower deuterated acetaldehydes which obscured the mass spectra results was particularly serious with $PdCl_2$. Apparently the Pd(0) precipitated in the course of reaction and caused the formation of monodeuterated ethylene as well as catalyzed cis–trans isomerization. The infrared spectra of the unreacted gases in runs with *trans*-$C_2H_2D_2$ indicated the presence of *cis*-$C_2H_2D_2$ and C_2H_3D. One run at a reaction time of 2 min gave a **4**/**3** ratio of 1.70. At times of 1 hr the ratio fell to 1.33.

In the Tl(III) runs no such isomerization or exchange of *trans*-$C_2H_2D_2$ was observed.

Kinetic Runs.—A constant-volume reactor was used for these studies. The apparatus and procedure have been described.[7] As reported previously, the kinetics of undeuterated ethylene followed the expected second-order kinetics [first order in Tl(III) and first order in C_2H_4)]. The value of k_2 at 25° and 0.5 *M* $HClO_4$ was found to be 0.63 $M^{-1}\ \mathrm{sec}^{-1}$, a value consistent with results at atmospheric ethylene pressure.[9] In the present study the value of k_2 was determined using ethylene-d_4. The initial ethylene pressure was about 70 mm. The value of k_2 for duplicate runs were 0.76 and 0.82 $M^{-1}\ \mathrm{sec}^{-1}$.

Registry No.—Palladium, 7440-05-3; thallium, 7440-28-0; ethylene, 74-85-1; *cis*-ethylene-d_2, 2813-62-9; *trans*-ethylene-d_2, 1517-53-9; acetylene, 74-86-2; ethylene-d_4, 683-73-8; D_2O, 7789-20-0.

Acknowledgment.—The author gratefully acknowledges the experimental assistance of Mr. R. H. Friant, who interpreted the mass spectral work, and Mr. F. Kriss, who did the majority of the laboratory work.

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[16] P. P. Nicholas and R. T. Carroll, *J. Org. Chem.*, **33**, 2345 (1968).

[17] P. M. Henry, *J. Amer. Chem. Soc.*, **93**, 3853 (1971).

[18] R. K. Brinton and F. E. Blacet, *J. Chem. Phys.*, **17**, 797 (1949).

Vapor-Phase Catalytic Dienol Dehydration. Influence of Various Metal Oxides on Product Distribution[1]

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trans-1,5-Heptadien-4-ol was dehydrated over Al_2O_3, WO_3, and ZrO_2 at 250°, yielding 3-*trans*,5-*trans*-, and 3-*cis*,5-*trans*-1,3,5-heptatriene as primary dehydration products and methyl-1,3-cyclohexadienes resulting from thermal cyclization of the cis,trans isomer. 1,3,6-Heptatriene, arising from 1,4 dehydration, was also obtained in significant amounts from both WO_3 and ZrO_2. Tungsten oxide is much more reactive than either Al_2O_3 or ZrO_2 both as a dehydration catalyst and subsequently in causing isomerization of the dehydration products. Both ZrO_2 and WO_3 yield significantly higher 3-cis/3-trans isomer ratios, in the product trienes, than has previously been reported for alumina.

Recent investigations[2–4] of various aspects of the

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[1] Supported in part by a National Science Foundation Student Science Training Program Grant, GW-6564. The author acknowledges the assistance of two students, Kevin Bennet and Patricia Maier.

[2] C. Spangler, *J. Org. Chem.*, **31**, 346 (1966).

[3] C. Spangler and N. Johnson, *ibid.*, **34**, 1444 (1969).

[4] C. Spangler and R. Hennis, *ibid.*, **36**, 917 (1971).

TABLE I

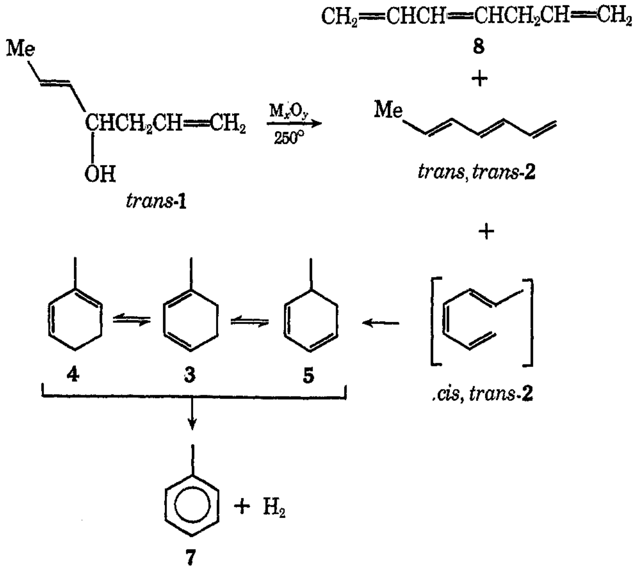
DEHYDRATION OF *trans*-1,5-HEPTADIEN-4-OL (1)

Catalyst[a,b] (column length, cm)	% recovery	Products, % of total[c]											
		trans,-trans-**2**	*cis,-trans*-**2**	*trans,-cis*-**2**	cis/trans[d]	cis/trans[e]	**3**	**4**	**5**	**6**	**7**	**8**[f]	**1**
A (25)	70[g]	36.5	23.7	3.3	0.6	1.3	2.3		24.6			8.0	
B (25)	74	46.0	10.3	3.1	0.2	1.0	0.9	0.5	36.0	1.0	1.1	1.0	
C (25)	76	23.5	23.9	3.2	0.9	1.8	1.2	1.4	19.1	0.9		24.6	
D (25)	60	13.3	8.4	1.8	0.6	2.9	11.6	11.5	11.7	2.0	4.3	13.8	
A (15)	79	21.4	12.9		0.6	0.9			6.5				58.8
C (15)	86	9.1	21.5		2.4	2.4						19.4	49.2
D (15)	70	31.2	35.4		1.1	1.3	3.2		1.3			25.2	1.2
D (15), 200°	72	30.6	36.0		1.2	1.2	0.7		1.3			27.4	3.0

[a] Catalyst A is Houdry HA-100S (γ-Al_2O_3, Houdry Process and Chemical Co.); B is KA-101 alumina (Kaiser Chemicals); C is zirconium oxide (98% ZrO_2, Strem Chemicals); D is tungsten oxide (95% WO_3, Strem Chemicals). [b] All dehydrations were carried out at 250° except as indicated. [c] For totals less than 100%, the balance is composed of unidentified low-boiling products. [d] Ratio of 3,4-cis configuration to 3,4-trans configuration, produced by dehydration. [e] [3,4-cis + cyclization products] to 3,4-trans ratio. [f] 1,3,-Heptatriene produced by dehydration. [g] Percentage yield based on complete dehydration, corrected for any residual alcohol and dehydrogenation in the product distribution (*e.g.*, toluene).

SCHEME I

METAL OXIDE CATALYZED DEHYDRATION OF *trans*-1,5-HEPTADIEN-4-OL



catalytic dehydration of substituted hexadienols have concentrated on the mechanism of alumina-catalyzed dehydration at elevated (200–400°) temperature. Alumina dehydration of *trans*-1,5-heptadien4-ol (**1**) yields 1,3,5-heptatriene (**2**), 1-, 2-, and 5-methyl-1,3-cyclohexadiene (**3**, **4**, and **5**), methylenecyclohexene (**6**), and toluene (**7**). The latter two products are usually produced only in small quantities. The product distribution is consistent with simple elimination to yield a mixture of cis and trans isomers about the incipient 3,4 double bond of 1,3,5-heptatriene, followed by electrocyclic ring closure of the central cis isomers and alumina-catalyzed isomerization of the resultant 5-methyl-1,3-cyclohexadiene. It has also been shown[4] that thermal isomerization of the methyl-1,3-cyclohexadienes *via* [1,5] sigmatropic hydrogen migration is not important under nonequilibrium fast-flow conditions, even though alumina-catalyzed isomerization is extensive.

Several metal oxides other than alumina have been utilized in catalytic dehydration of alcohols; however, none have been utilized for dienol dehydration. In the light of the apparent complexity of the alumina process, we investigated two other common metal oxides, zirconium oxide (ZrO_2) and tungsten oxide (WO_3), as potentially useful catalysts in dienol dehydration studies. In particular we were interested in the cis–trans isomer distribution in the newly introduced double bond, and the overall product distribution.

In the present study, *trans*-1,5-heptadien-4-ol (**1**) was dehydrated over alumina (two different types), zirconium oxide, and tungsten oxide at 250°. Two different alumina catalysts were utilized to explore the presence or absence of specific catalytic effect on the product distribution. Conversions of **1** to products varied from 50% to complete dehydration, thus allowing an estimation as to whether product distributions varied significantly with percentage conversion. Product distributions for the four catalysts are shown in Table I. The results indicate that all four catalysts follow the same general reaction scheme (Scheme I), except that a nonconjugated triene, 1,3,6-heptatriene (**8**), is a major dehydration product when either WO_3 or ZrO_2 is utilized. It is also significant that WO_3 appears to exhibit much greater reactivity than either Al_2O_3 or ZrO_2, yielding essentially complete dehydration under conditions which yield only 50% conversion with the other catalysts.

The relative yields of cis and trans configurations about the incipient 3,4 double bond were of particular interest. As previously shown,[3] alumina-catalyzed dehydration shows little cis–trans preference. In confirmation of this, both alumina catalysts employed in the present study show ratios close to unity, once corrections are made for the amount of cyclization product obtained. However, both zirconium oxide and tungsten oxide preferentially yield a cis configuration under conditions of complete dehydration. Although the two trienes formed as primary dehydration products have *trans,trans*-**2** and *cis,trans*-**2** configurations under conditions of complete dehydration a third isomer, *trans,cis*-**2**, also appears, probably as a result of isomerization of the trans,trans isomer. In order to determine if the observed 3,4-cis/3,4-trans product ratio was a measure of the nature of the dehydration transition state, or the result of catalyst-induced on-column isomerization after dehydration,

TABLE II
THERMOLYSIS OF 1,3,5-HEPTATRIENE[a]

Catalyst/ support[b]	Recovery, %	Products, % of total *trans,-trans*-**2**	*cis,-trans*-**2**	*trans,-cis*-**2**	cis/ trans[d]	cis/ trans[e]	**3**	**4**	**5**	**6**	**7**	**8**[f]
A	77	53.3	36.2	6.0	0.61	0.69			4.5			
B	75	52.9	26.3	7.4	0.44	0.66	0.9		12.5			
C	77	51.3	33.1	6.7	0.58	0.69	0.2		6.7			
D[c]	70	30.7	22.7	5.7	0.78	1.16	4.9	4.9	5.4	1.5	4.1	8.9
Pyrex helices	85	54.0	32.4	7.3	0.53	0.63	0.3		6.0			

[a] All thermolyses carried out with 3.0-g samples at 250° and a starting composition of 54.8% *trans,trans*-**2**, 37.2% *cis,trans*-**2**, and 8.0% *trans,cis*-**2** (cis/trans = 0.60). [b] All columns packed to a depth of 15 cm. [c] In addition, 8.7% of monoolefinic and 2.5% of a mixture of six low-boiling components were also present. [d] Ratio of 3,4-cis configuration produced by thermal and/or catalytic isomerization. [e] [3,4-cis + cyclization products] to 3,4-trans ratio. [f] 1,3,6-Heptatriene produced by catalytic isomerization.

TABLE III
THERMOLYSIS OF 1,3,6-HEPTATRIENE (**8**)[e]

Catalyst[a] (temp, °C)	Recovery, %	Products, % of total *trans,-trans*-**2**	*cis,-trans*-**2**	*trans,-cis*-**2**	**3**	**4**	**5**	**8**
A (250)	75[b]	33.0	12.0	2.1			Trace	51.5
C (250)	72[b]	7.8	3.5	Trace	1.5		Trace	87.0
D (200)	70[c]	7.5	8.5	Trace	1.3		1.5	76.5
D (250)	60[c,d]	7.2	4.2	1.2	6.9	6.4	7.1	26.9

[a] All columns packed to a depth of 15 cm. [b] Thermolyses carried out with 1.0-g samples at 250° and a starting trans-sample purity of 99% (glpc). [c] Thermolyses carried out with 5.0 g-samples at 250°. [d] Toluene (12%) and several unidentified low-boiling products were also obtained. [e] Chemical Samples Co.

pure 1,3,5-heptatriene (**2**) was thermolyzed under dehydration conditions, and the results are shown in Table II. Alumina and zirconium oxide show little difference in their behavior and the cis–trans ratio does not change significantly upon thermolysis. Tungsten oxide again demonstrates its increased reactivity in that the ratio increases to 1.16 from a starting value of 0.60. It could be argued that the lack of change in the 1,3,5-heptatriene cis/trans ratio upon thermolysis over catalysts A, B, and C (Table II) would prove little if the isomers had already achieved thermal equilibrium. Recently, James and Egger[5] and coworkers have shown that the equilibrium lies in the range 0.2–0.4 in the temperature range 171–254°. Thus it would appear that little isomerization occurs at 250° over Al_2O_3 or ZrO_2, and that the cis/trans products ratio is indicative of the nature of the transition state. Appreciable isomerization occurs over WO_3, yielding a product distribution that parallels the dehydration distribution in both identity and complexity.

An interesting difference between the compositions obtained from alumina, zirconium oxide, and tungsten oxide is the presence of large quantities of the unconjugated triene, 1,3,6-heptatriene (**8**). This product is most probably obtained *via* 1,4 dehydration of **1**, although isomerization of the conjugated isomer cannot be precluded. We favor the former interpretation not only from the thermolytic behavior of **2** on the various catalysts (Table II), but also on the observation that **8** is formed in large quantity for both partial and complete dehydration. Thus **8** appears to be a primary dehydration product of **1**. Nazarov and Mavrov[6] have observed similar behavior in the dehydration of various allyl and vinyl carbinols over ZrO_2/pumice, where they obtained nonconjugated products in quantities ranging from 18 to 21%. In an attempt to estimate whether the quantities of **8** obtained were an accurate measure of primary 1,4 dehydration, **8** was thermolyzed at 250° over Al_2O_3, ZrO_2, and WO_3 under conditions identical with those employed during dehydration (Table III). Tungsten oxide again demonstrated the greatest catalytic activity (73% isomerization) at 250° and the lowest percentage recovery of volatile products. Even at 200° WO_3 demonstrates a greater reactivity than ZrO_2 (24% isomerization). Isomerization to **2**, the conjugated triene, was extensive (47%) for Al_2O_3, and less so for ZrO_2 (11%). This may well explain why recovery percentages are, in general, considerably lower for WO_3 than for the other two catalysts. Thus it is probable that 1,4 dehydration is actually more important for all the catalysts employed in this study than the product distribution alone would indicate.

Several general conclusions can be drawn from the above studies. We find the action of both Al_2O_3 and ZrO_2, with the exception of 1,4 dehydration, to be quite similar, as are their reactivities. Tungsten oxide appears to be much more reactive and prone to secondary catalytic reactions with the primary dehydration products. Both ZrO_2 and WO_3 yield substantially higher cis/trans product ratios than for Al_2O_3, which indicates different steric requirements in the transition state. In this respect, both ZrO_2 and WO_3 are more closely related to ThO_2, for which a concerted cis elimination *via* a cyclic transition state has been proposed.[7] Such transition states are usually formed to preferentially minimize steric interactions and bring a larger portion of the molecule closer to the catalyst surface. Thus dehydration of 2-butanol or 2-octanol over ThO_2 at 350–450° yields predominantly 1 olefins[7] by eliminating a terminal methyl proton in preference to an interior secondary methylene proton. This may indeed explain the relatively large quantities of 1,4-dehydration products that are observed for both ZrO_2 and WO_3.

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(5) T. James and K. Egger, *J. Chem. Soc. B*, 348 (1971).

(6) I. N. Nazarov and M. U. Mavrov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 365 (1958); *Chem. Abstr.*, **52**, 12746*d* (1958).

(7) A. J. Lundeen and R. Van Hoozer, *J. Amer. Chem. Soc.*, **85**, 2180 (1963).

Experimental Section[8]

Nature of Catalysts.—Catalyst A[9] (Houdry HA-100s) is a γ-alumina catalyst which has been described as essentially nonacidic, and has been utilized as a dehydration catalyst in a large number of published examples[10] by several different workers. Catalyst A has a sodium content of 0.1–0.2% and was utilized in the form of 0.125-in. pellets.

Catalyst B[11] (Kaiser Chemicals, KA-101) is a quasiamorphous alumina, as determined by X-ray diffraction,[12] which can be referred to as χ,ρ-alumina. The X-ray pattern is diffuse and intermediate between amorphous ρ and the more crystalline χ, but distinct from each. A minor phase (*ca.* 20–30%) which coexists with the above dominant phase resembles γ-alumina, but is more diffuse. The catalyst is supplied as pellets, 8–14 mesh, with a surface area of 360 m^2/g. Sodium content is 0.40%, expressed as Na_2O.

Catalyst C[13] is catalytic zirconium oxide, containing 98% ZrO_2 and 2% alumina with a surface area of 50 m^2/g and a pore volume of 0.21 cc/g, supplied as 0.125-in. pellets.

Catalyst D[13] is catalytic tungsten oxide, containing approximately 95% WO_3 with a surface area of 17 m^2/g and a pore volume of 0.19 cc/g.

Catalysts were prepared by heating at the dehydration temperature for a period of 1 hr under reduced pressure (20–25 mm) in a nitrogen atmosphere. Fresh samples of catalyst were used in each run. After this pretreatment they were used directly as described below.

Dehydration of *trans*-1,5-Heptadien-4-ol (1).—*trans*-1,5-Heptadien-4-ol[14] (10 g, 0.09 mol) was added dropwise at a rate of 0.25 ml/min through a 22-mm Pyrex tube packed to a depth of either 15 or 25 cm with catalyst and externally heated with a Lindberg Hevi-Duty split-tube furnace. A pressure of 20–25 mm was maintained in the system to facilitate rapid removal of the product from the column. The product was trapped in a flask immersed in a Dry Ice–acetone bath, and subsequently warmed to room temperature, washed with water, filtered through anhydrous magnesium sulfate, and analyzed immediately by glpc (see Table I for product analyses). No attempt was made to maximize the yields.

The dehydration products were identified by collecting each peak emanating from the chromatograph in glass V tubes immersed in cooling baths: (a) in isooctane for uv analysis, and (b) in $CDCl_3$ for nmr analysis. In each case, the product was identified by comparison of the uv, nmr, and glpc retention times to those of authentic samples in our laboratories.

Registry No.—**1,** 24581-03-1; **8,** 1002-27-3; 1,3,5-heptatriene, 2196-23-8; Al_2O_3, 1344-28-1; ZrO_2, 1314-23-4; WO_3, 1314-35-8.

(8) Gas–liquid partition chromatography was performed with an Aerograph Model 202-1B dual column instrument equipped with a Hewlett-Packard Model 3370-A electronic integrator for peak area measurement; dual 15-ft 15% TCEP on 60/80 mesh Chromosorb W columns were utilized for analysis. Ultraviolet spectra were obtained with a Perkin-Elmer Model 202, nmr spectra with a Varian A60-A using TMS as an internal standard ($CDCl_3$ solvent). All compounds were identified by both uv and nmr spectra and glpc retention times and comparison to authentic samples.

(9) Houdry Process and Chemical Co.

(10) See, for example, L. Klemm, J. Shabtai, and D. Taylor, *J. Org. Chem.*, **33**, 1480 (1968), and references cited therein.

(11) Kaiser Chemicals, Division of Kaiser Aluminum and Chemical Corp.

(12) Private communication, Dr. Robert B. Emerson, Staff Research Associate, Chemical Aluminas, Kaiser Chemicals, Box 1031, Baton Rouge, La.

(13) Strem Chemicals, Inc.

(14) C. Spangler and G. F. Woods, *J. Org. Chem.*, **30**, 2218 (1965).

Photochemical Deoxygenation of Aryl Sulfoxides

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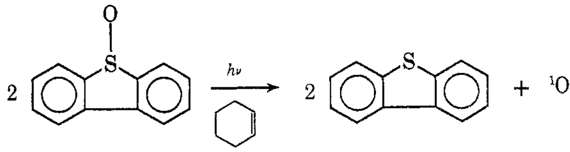
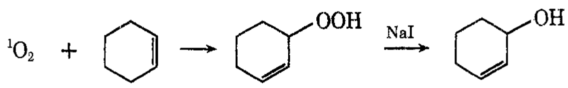
Several selective and mild chemical methods have recently been reported for reduction of sulfoxides to the corresponding sulfides.[2] To supplement these reports, we wish to communicate the photodeoxygenation of some aryl sulfoxides in good yields.

Kharasch and Khodair[3] found that diphenyl sulfoxide on direct photolysis in benzene gave biphenyl (53%), diphenyl sulfide (7%), and a small amount of diphenyl disulfide and that dibenzothiophene and dibenzothiophene dioxide were inert under these conditions. We find that in nonaromatic solvents direct photolysis of the aryl sulfoxides in Table I gives good to excellent yields of the corresponding sulfides. Diphenyl and *p*-tolyl phenyl sulfides, however, are photolabile, giving several products,[3,4] so that the yields of sulfide are diminished. Nevertheless, sensitized photolysis of diphenyl and *p*-tolyl phenyl sulfoxides with triplet sensitizer benzophenone or acridine[5] gives only the corresponding sulfides as products[6] and indicates that the photoreduction probably proceeds *via* the triplet excited state.[5] In further support of this conclusion, it was found that piperylene[7] could effectively prevent the deoxygenation of diphenyl sulfoxide, for example.

To determine the fate of the oxygen lost, dibenzothiophene oxide was photolyzed in the presence of cyclohexene as a trap for singlet oxygen.[8] From the amount of 2-cyclohexen-1-ol obtained (glc yield), we find a minimum of 41% of the available oxygen in the sulfoxide reacting as $^1O_2$ (eq 1, 2).[9]



(1)



(2)

Photolysis of *dialkyl* sulfoxides[10] has been found to give mixtures of products, notably aldehydes and disulfides, but not dialkyl sulfides. Pyrolysis of dialkyl sulfoxides with available β hydrogens is known to give largely olefinic products and sulfenic acids.[11] If only α hydrogens are available a rearrangement of the sulfoxide and formation of aldehydic and sulfhydryl prod-

(1) NSF Predoctoral Fellow, 1970–1972.

(2) J. P. A. Castrillón and H. H. Szmant, *J. Org. Chem.* **30**, 1338 (1965); I. Granoth, A. Kalir, and Z. Pelak, *J. Chem. Soc. C*, 2424 (1969); D. W. Chasar, *J. Org. Chem.*, **36**, 613 (1971); T-L. Ho and C. M. Wong, *Syn. Commun.*, **3**, 37 (1973); H. C. Brown and M. Ravindran, *Synthesis*, 42 (1973).

(3) N. Kharasch and A. I. A. Khodair, *Chem. Commun.*, 98 (1967).

(4) W. Carruthers, *Nature (London)*, **209**, 908 (1966).

(5) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, pp 131, 132.

(6) Sulfide products can be easily purified from sensitizers and sulfoxides by tlc or column chromatography with silica gel.

(7) N. C. Yang, *J. Amer. Chem. Soc.*, **90**, 504 (1968); G. S. Hammond, P. A. Leermakers, and N. J. Turro, *ibid.*, **83**, 2396 (1961).

(8) K. Gollnick, *Advan. Photochem.*, **6**, 1 (1968).

(9) A referee has pointed out that formation of oxygen atoms seems more likely than direct formation of singlet molecular oxygen, and that sensitization by dibenzothiophene of $^3O_2$ formed in the reaction to singlet oxygen may account for the peroxide detected. Although our data do not permit unambiguous distinction between direct and indirect formation of singlet oxygen, the relatively good yield of peroxide formed and the absence of any products expected from cyclohexene and atomic oxygen [*e.g.*, epoxycyclohexane and cyclohexanone: T. Tsuchiya, H. Arai, and H. Igeta, *Tetrahedron Lett.*, 2747 (1969)] give some support to direct formation of singlet oxygen.

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