Anal. Calcd. for $C_{18}H_{20}SO_3$: C, 68.32; H, 6.37. Found: C, 68.20; H, 6.42.

3-Phenylcyclopentene.—A solution of sodium ethoxide prepared from 7 g. (0.3 g.-atom) of sodium and 500 ml. of absolute ethanol was heated to 80° under nitrogen. A solution of 31.2 g. (0.099 mole) of *trans*-2-phenylcyclopentyl tosylate in 500 ml. of absolute ethanol was added dropwise over 46 hr. The mixture was heated for 7 hr., cooled to room temperature, diluted with water, and extracted three times with petroleum ether (b.p. 35–37°). The extract was dried, concentrated, and distilled through a 12-in. spiral-packed rectifying column to give 5.5 g. (38.5%) of 3-phenylcyclopentene, b.p. 51.5–54° (1 mm.), $n^{20.6}$D 1.5415 [lit.[20] b.p. 92–93° (13 mm.), n^{19}D 1.5396]. This olefin is readily separated from the higher boiling 1-phenylcyclopentene by vacuum distillation or, for analytical purposes, by gas chromatography.

Phenylcyclopentane was prepared by catalytic hydrogenation of 1-phenylcyclopentene over platinum in methanol; b.p. 49–53° (1 mm.), n^{20}D 1.5283 (lit.[21] b.p. 213–215°, nD 1.5320). This substance had the same retention time as 3-phenylcyclopentene on silicone or Carbowax gas chromatography columns; its infrared spectrum lacked a number of moderately strong peaks shown by that of the 3-olefin.

Hydrogenolysis of ***trans*****-2-Phenylcyclopentanol.**—In a flask fitted with an addition funnel, a magnetic stirrer, and a distilling head was placed 3.6 g. (0.0224 mole) of *trans*-2-phenylcyclopentanol. The system was flushed with nitrogen and 75 ml. of a 1.22 *N* hydride solution, prepared from 8.5 g. (0.224 mole) of lithium aluminum hydride and 180 g. (0.6 mole) of crystalline aluminum chloride in 800 ml. of ether, was added dropwise with stirring. The flask was then heated, distilling ether until the internal temperature reached 70°, which temperature was maintained for 24 hr. The mixture was cooled, diluted with ether, treated cautiously with water, and extracted with ether. Concentration gave 3.2 g. of a yellow oil which was distilled under vacuum. The distillate, b.p. 55–64° (1 mm.), amounted to 1.58 g., $n^{19.5}$D 1.5364, and gave an infrared spectrum indicating it to be slightly impure phenylcyclopentane. Analysis by v.p.c. showed two peaks, the first (89% of the total area) corresponding to phenylcyclopentane and the second (11% of the total area) to 1-phenylcyclopentene. The refractive index of the product is that to be expected of a mixture of 88% phenylcyclopentane and 12% 1-phenylcyclopentene, indicating that little or none of the 3-olefin is present.

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[20] J. von Braun and M. Kühn, *Ber.*, **60**, 2551 (1927).

[21] W. Borsche and W. Menz, *ibid.*, **41**, 205 (1908).

Dehydration of Alcohols, Diols, and Related Compounds in Dimethyl Sulfoxide[1]

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This report lists additional examples of the dehydration of alcohols (particularly 1-alkylcycloalkanols) to olefins, the dehydration of alcohols to ethers and certain diols to cyclic ethers, the pinacol rearrangement *vs.* diene formation from 1,2-diols, the dehydration and in part oxidation of two 1,3-diols, the conversion of ethers to olefins, and the preparation of furans from 1,4-diketones. Additional observations on the mechanism are discussed.

The initial report of the dehydration of alcohols in dimethyl sulfoxide described the scope of the reaction as limited to secondary and tertiary benzylic alcohols and tertiary aliphatic alcohols.[3] In view of the stereochemistry of the elimination in *erythro-* and *threo*-1,2-diphenyl-1-propanol and other data, the mechanism of this dehydration appeared to involve carbonium ions.[3] In this paper we wish to extend the scope of this reaction and offer additional comments about the mechanism.

The previous paper in this series noted several examples of primary and secondary alcohols which failed to dehydrate[3]; among these was 1-phenyl-2-propanol. However, when this alcohol was heated in dimethyl sulfoxide at 190° for 48 hr. under nitrogen, 41% of 1-phenylpropene, 49% of unchanged alcohol, and less than 1% of phenylacetone were found. Performing the reaction in air caused the formation of appreciable amounts of phenylacetone (25%). This example represents the first successful dehydration of a simple secondary alcohol in dimethyl sulfoxide. Additional cases of dehydration of primary and secondary alcohols in polyfunctional compounds will appear later.

The newest group of tertiary alcohols capable of dehydration in dimethyl sulfoxide are the 1-alkylcycloalkanols, and data concerning these examples are listed in Table I. Analysis of the olefin composition was by v.p.c. while identification of these products employed various combinations of physical constants, infrared spectra, and/or n.m.r. spectra. The major product in each of these reactions was the endocyclic olefin, 1-alkylcycloalkene. In the case of 1-methylcyclohexanol, dehydration in dimethyl sulfoxide produced an olefin mixture (1-methylcyclohexene and methylenecyclohexane) similar with that obtained from an iodine- or *p*-toluenesulfonic acid[4]-catalyzed dehydration. The result remains consistent with a carbonium ion intermediate in the dimethyl sulfoxide dehydration. The appearance of 2-cyclohexylpropene from 1-isopropylcyclohexanol requires double bond migration which can be accommodated by intermediate carbonium ions.

The dehydration of 1,2-diphenylethanol in dimethyl sulfoxide produced *trans*-stilbene (93%) and unchanged alcohol (5%).

When a series of experiments was performed on the dehydration of 1-phenyl-1-propanol in varying amounts of dimethylsulfoxide, a new mode of dehydration was observed, namely, ether formation. These data are summarized in Table II and show that, in the presence of small amounts of dimethyl sulfoxide, ether production is favored. Control experiments ruled out a thermal

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for support of this research.

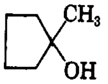
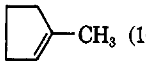
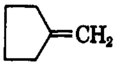
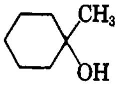
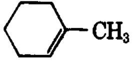
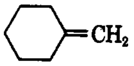
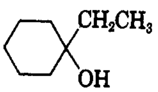
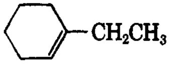
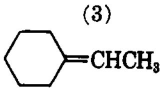
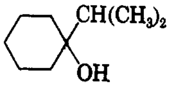
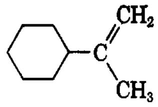
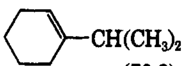
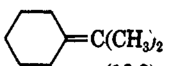
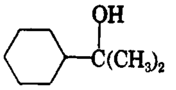
[2] Abstracted from part of the Ph.D. dissertation of W. L. H., submitted in July, 1963.

[3] V. J. Traynelis, W. L. Hergenrother, J. R. Livingston, and J. A. Valicenti, *J. Org. Chem.*, **27**, 2377 (1962).

[4] A. C. Cope, C. L. Bumgardner, and E. E. Schweizer, *J. Am. Chem. Soc.*, **79**, 4732 (1957). These workers reported the dehydration of 1-methylcyclohexanol and other 1-methylcycloalkanols by treatment with *p*-toluenesulfonic acid and found 2–5% of the exocyclic olefin in their product mixture.

TABLE I

THE DEHYDRATION OF 1-ALKYLCYCLOALKANOLS

Alcohol	Olefin yield, %	Olefin composition[a]		
	88	 (100)	 (0)	
	74.5	 (95)	 (5)	
	60[b]	(95)	(5)	
	37[c]	(97)	(3)	
	55.5	 (94)	 (6)	
	62	 (5.4)	 (78.3)	 (16.3)
	57	(72.8)	(0)	(27.2)

[a] The olefin composition was determined by v.p.c. [b] Iodine-catalyzed dehydration. [c] Dehydration by a trace of *p*-toluenesulfonic acid

TABLE II

THE DEHYDRATION OF 1-PHENYL-1-PROPANOL IN VARYING AMOUNTS OF DIMETHYL SULFOXIDE[a]

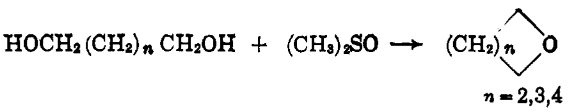
Alc:dimethyl sulfoxide mole ratio	Product composition[b] $C_6H_5CH=CHCH_3$	$C_6H_5\overset{O}{\overset{\|}{C}}CH_2CH_3$	$C_6H_5\overset{OH}{\overset{\mid}{C}H}CH_2CH_3$	$C_6H_5\overset{C_2H_5}{\overset{\mid}{C}H}O\overset{C_2H_5}{\overset{\mid}{C}H}C_6H_5$
1:8	89	6	6	0
1:3	80	5.5	7	7
1:1	56	8	4	34
3:1	30	3	14	53

[a] These reactions were run at 175° for 9 hr. [b] The product composition was determined by v.p.c., for the product residue isolated in essentially quantitative yield. The starting alcohol was stable to the conditions used for v.p.c.

dehydration leading to either the olefin or ether. Identification of 1-phenylpropyl ether was accomplished by physical constants, the infrared spectrum, and the n.m.r. spectrum, which also revealed that the ether was a mixture of two components, most likely the *meso* and *dl* isomers. Table III lists the n.m.r. data for benzyl ether, α-phenethyl ether, and 1-phenylpropyl ether.

The previous report[3] described the thermal dehydration and dimethyl sulfoxide dehydration of *threo*-1,2-diphenyl-1-propanol and cited the isolation of an unidentified solid and oil. These materials have now been identified as a mixture of isomers of 1,2-diphenyl-1-propyl ether on the basis of their infrared spectra and n.m.r. spectra (see Table III).

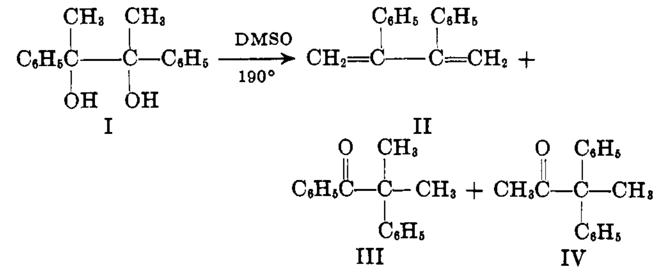
These observations of ether formation suggested the possibility of preparing cyclic ethers by the dehydration of certain diols. This reaction recently has been applied by Gillis and Beck[5] toward the synthesis of a variety of substituted tetrahydrofurans in yields of 50–98%. By way of addition to these examples, we wish to report the conversion of 1,4-butanediol, 1,5-pentanediol, and 1.6-hexanediol, using 2 moles of alcohol per mole of dimethyl sulfoxide, to the corresponding heterocycles, tetrahydrofuran (70%), tetrahydropyran (47%), and oxepane (24%). Characterization of these products was by physical constants and comparison of retention times in v.p.c. and infrared spectra with authentic samples.



$HOCH_2(CH_2)_nCH_2OH + (CH_3)_2SO \rightarrow$ $(CH_2)_n$ O, $n = 2,3,4$

A second series of diols investigated were the pinacols and other 1,2-diols which provided information on the pinacol rearrangement *vs.* diene formation. In these reactions the operating temperature was 160°–190° with a time variation of 7–48 hr. When 1-phenyl-1,2-ethanediol was heated at 190° for 48 hr., the major product was phenylacetaldehyde (64%) isolated as the 2,4-dinitrophenylhydrazone derivative. A solution of 2-methyl-2,3-butanediol in dimethyl sulfoxide, after 36 hr. at 190°, produced 3-methyl-2-butanone (66%) isolated by distillation. In these two cases only pinacol rearrangement products were observed; of course, in the first example, diene formation was not possible.

With the pinacols, both diene and rearranged ketones were found and in some cases the diene was the major product. The reaction of 2,3-diphenyl-2,3-butanediol (a mixture of *meso* and *dl*) and dimethyl sulfoxide for 14 hr. at 190° gave 2,3-diphenylbutadiene (II, 17%) and a 65% yield of ketones composed of 11% 1,2-diphenyl-2-methyl-1-propanone (III) and 89% 3,3-diphenyl-2-butanone (IV). The ketone analysis was by v.p.c.



$$\underset{\text{I}}{C_6H_5\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-C_6H_5} \xrightarrow[190^\circ]{DMSO} \underset{\text{II}}{CH_2=\overset{C_6H_5}{C}-\overset{C_6H_5}{C}=CH_2} +$$

$$\underset{\text{III}}{C_6H_5\overset{O}{\overset{\|}{C}}-\underset{C_6H_5}{\overset{CH_3}{C}}-CH_3} + \underset{\text{IV}}{CH_3\overset{O}{\overset{\|}{C}}-\underset{C_6H_5}{\overset{C_6H_5}{C}}-CH_3}$$

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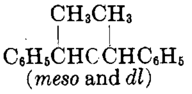
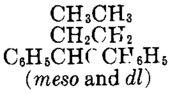
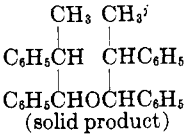
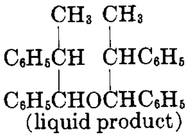
(5) B. T. Gillis and P. E. Beck, *J. Org. Chem.*, **28**, 1388 (1963).

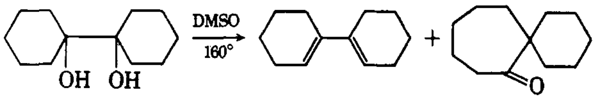
TABLE III

NUCLEAR MAGNETIC RESONANCE SPECTRA OF SOME BENZYL ETHERS[a]

Compound	Peak description	τ-Values		Weight	Proton assignment
$C_6H_5CH_2OCH_2C_6H_5$	Singlet		2.80	10	Benzene
	Singlet		5.58	4	Methylene
		A[a]	B[b]		
 $C_6H_5\overset{CH_3}{\overset{\vert}{C}}HC\overset{CH_3}{\overset{\vert}{C}}HC_6H_5$ (*meso* and *dl*)	Singlet	2.82	2.76	10	Benzene
	Quartet center	5.56[c]	5.85[c]	2	Methine
	Doublet center	8.57[c]	8.67[c]	6	Methyl
		C[d]	D[d]		
 $C_6H_5\overset{CH_3}{\overset{CH_2}{C}}HC\overset{CH_3}{\overset{CH_2}{C}}F_6H_5$ (*meso* and *dl*)	Singlet	2.95	2.85	10	Benzene
	Triplet center	5.86[e]	6.08[e]	2	Methine
	Multiplet center	8.21	8.50	4	Methylene
	Triplet center	9.17[f]	9.25[f]	6	Methyl
 $\begin{array}{l} \quad CH_3\ \ CH_3{}^{j} \\ \quad\ \vert \qquad\ \vert \\ C_6H_5CH\ \ CHC_6H_5 \\ \quad\ \vert \qquad\ \vert \\ C_6H_5CHOCHC_6H_5 \end{array}$ (solid product)	Multiplet center	3.03		10	Benzene
	Doublet center	5.88[g]		2	O-Methine
	Multiplet center	6.94		2	C-Methine
	Doublet center	8.66[h]		6	Methyl
		E[i]	F[i]		
 $\begin{array}{l} \quad CH_3\ \ CH_3 \\ \quad\ \vert \qquad\ \vert \\ C_6H_5CH\ \ CHC_6H_5 \\ \quad\ \vert \qquad\ \vert \\ C_6H_5CHOCHC_6H_5 \end{array}$ (liquid product)	Multiplet center	3.03		10	Benzene
	Doublet center	6.05[g]	5.82[g]	2	O-Methine
	Multiplet center	7.00		2	C-Methine
	Doublet center	9.11[h]	8.68[h]	6	Methyl

[a] These spectra were determined in carbon tetrachloride solution with tetramethylsilane as an internal standard. [b] Analysis of components A and B was by comparison of the relative peak areas for the methine proton. This was found to be 37% A and 63% B. [c] J = 6.8 c.p.s. [d] Analysis of components C and D was by comparison of the relative peak areas for the methine proton. This was found to be 46% C and 54% D. [e] J = 6.1 c.p.s. [f] J = 7.3 c.p.s. [g] J = c.p.s. [h] J = 7 c.p.s. [i] Analysis of components E and F was by comparison of the relative peak areas for the O-methine proton. This was found to be 25% E and 75% F. [j] The unknown solid from the dehydration of *threo*-1,2-diphenyl-1-propanol was recrystallized several times from petroleum ether (b.p. 60–90°) and had m.p. 151–154.5°. *Anal.* Calcd. for $C_{30}H_{30}O$: C, 88.63; H, 7.44. Found: C, 88.60, 88.68; H, 7.40, 7.55.

and the product identification involved physical constants, infrared spectra, and solid derivatives. When a second reaction was processed after 7 hr. at 190°, 15% diene II, 33% ketones (19% III and 81% IV), 33% pure *dl* diol I, and 14% diol I (mixture of *meso* and *dl*) were found. This procedure provides a convenient method for preparing the pure *dl* diol I. When the dehydrations were performed with *dl* diol I for 14 hr. and pure *meso* diol I for 7 hr., similar results were obtained, 12% and 15% diene II, 65% ketones (2% III and 98% IV), and 68% ketones (2.4% III and 97.6% IV), respectively. These data point out the greater reactivity of the *meso* compound toward rearrangement. Although the rearrangement of pure *dl* diol I and *meso* diol I in sulfuric acid has been described,[6] no mention was made of the relative ease of rearrangement of the two diastereomers and the only product reported was ketone IV. The dehydration of pinacol itself was performed at several temperatures with little effect on the ratio of products. When pinacol and dimethyl sulfoxide were heated at 160°, 175°, and 185°, the products which distilled from the reaction vessel were 2,3-dimethylbutadiene, 52%, 56%, and 55%; and pinacolone, 20%, 27%, and 30%, respectively. Bicyclohexyl-1,1′-diol (V) was heated in dimethyl sulfoxide at 160° for 16 hr. and gave bicyclohexyl-1,1′-diene (VI, 85%), spiro[5.6]dodecan-7-one (VII, 4%), and an unidentified component. The mixture composition was analyzed by v.p.c. and the diene was conveniently purified by column chromatography on alumina.



V VI VII

The dehydration of two 1,3-diols also has been observed. In the case of 2-methyl-2,4-pentanediol, the products isolated were 49% of a mixture of 2-methylpentadienes and 29% of 2-methyl-1-penten-4-ol. This diol contains both a tertiary and secondary hydroxyl group and, if the tertiary alcohol dehydrates first, this could lead to 2-methyl-1-penten-4-ol or 2-methyl-2-penten-4-ol. The latter compound now has an allylic hydroxyl which may dehydrate to a diene. Subsequent isomerization of the diene could explain the mixture observed. The suggestion of a facile dehydration of allylic alcohols is based on the present scope of this reaction; tertiary and benzylic alcohols dehydrate under conditions where primary and secondary alcohols fail. However, 2-methyl-1-penten-4-ol was subjected to the same reaction conditions as for the parent diol and produced a mixture of 2-methylpentadienes in 55% yield. Whether this alcohol dehydrated directly or was first isomerized to 2-methyl-2-penten-4-ol is not known. When 1,3-butanediol (containing a secondary and primary hydroxyl) was heated at 190° for 48 hr., the products isolated were crotonaldehyde (26%) and 2-buten-1-ol (54%). This example provided an interesting case where both an oxidation and

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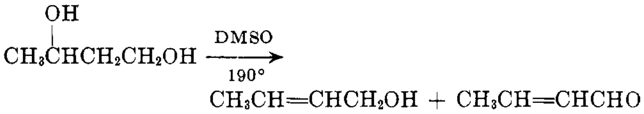
[6] M. Ramart-Lucas and M. E. Salmon-Legagneur, *Bull. soc. chim. France*, [4] **45**, 718 (1929); M. Ramart-Lucas and M. Biguard, *Compt. rend.*, **194**, 189 (1932).

TABLE IV

DIMETHYL SULFOXIDE DEHYDRATION OF ALCOHOLS IN THE PRESENCE OF BASE

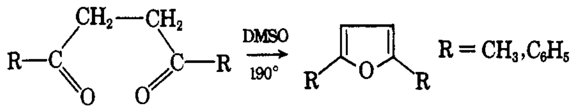
Alcohol (moles)		Dimethyl sulfoxide, moles	Base (moles)		Yield, %	
5-Butyl-5-nonanol	(0.053)	0.371	$C_6H_5NH_2$	(0.005)	5-Butyl-4-nonene (94)	Recovered alcohol (0)
	(0.0158)	0.110		(0.0158)	(91)	(1)
	(0.0158)	0.110		(0.110)	(79)	(8)
	(0.158)	0.110	n-$C_8H_{17}ONa$	(0.0158)	(98)	(0)
2-Methyl-2-hexanol	(0.0258)	0.181		(0.0026)	45% 2-Methyl-1-hexene 55% 2-Methyl-2-hexene (84)	
	(0.0058)	(0.40)	$C_6H_5NH_2$	(0.0058)	45.5% 2-Methyl-1-hexene 54.5% 2-Methyl-2-hexene (85)	



$$CH_3\overset{\overset{OH}{|}}{C}HCH_2CH_2OH \xrightarrow[190^\circ]{DMSO} CH_3CH{=}CHCH_2OH + CH_3CH{=}CHCHO$$

dehydration occurred with the dehydration involving a secondary alcohol. To account for the origin of crotonaldehyde two alternatives were available, dehydration followed by oxidation or oxidation followed by dehydration. In order to decide between these possibilities, the two intermediates were subjected to the reaction conditions. 2-Buten-1-ol distilled from the reaction mixture with no crotonaldehyde while aldol was converted to crotonaldehyde (64%) in only 6 hr. Another example of a facile dehydration of a β-hydroxycarbonyl system is the conversion of diacetone alcohol in dimethyl sulfoxide at 190° for 8 hr. to mesityl oxide (81%).

Some miscellaneous examples which bear on the scope of this reaction involve the conversion of ethers to olefins and the synthesis of furans. 4-Methoxy-4-methyl-2-pentanone readily lost methanol upon heating in dimethyl sulfoxide to afford mesityl oxide (90%). When α-methylbenzyl ether was heated in dimethyl sulfoxide at 175° for 9 hr., polystyrene was isolated in 38% yield. In the previous paper[3] it was shown that when styrene was formed by dehydration of α-phenethyl alcohol in dimethyl sulfoxide, it polymerized. The conversion of acetonylacetone and 1,4-diphenyl-1,4-butanedione to 2,5-dimethylfuran and 2,5-diphenylfuran in 66% and 60% yield, respectively, suggests this procedure as a potential method of furan synthesis.[7] This approach enjoys the advantage that nonacidic conditions are employed and thus possible side reactions of alkylfurans are reduced.



In considering the various mechanisms for the dehydration of alcohols in dimethyl sulfoxide, a simple thermal elimination of water was excluded in previous work.[3] An acid-catalyzed elimination was considered as a possibility. Although precautions were taken to exclude acidic and other contaminants in dimethyl sulfoxide, this substance undergoes some decomposition upon prolonged heating at the reaction temperatures.[8] A study of the direction of elimination in t-pentyl alcohol and 2-methyl-2-hexanol[3] did not permit one to discard an acid-catalyzed mechanism. We now wish to report the reaction of 5-n-butyl-5-nonanol and 2-methyl-2-hexanol in dimethyl sulfoxide with aniline or sodium n-octoxide added. The results reported in Table IV reveal that neither base has any appreciable effect on the yield of olefins or the direction of elimination. This removes the possibility of an acid-catalyzed dehydration. In the previous paper[3] the stereochemistry of *erythro-* and *threo*-1,2-diphenyl-1-propanol favored a carbonium ion intermediate, and support for this path is now available from the several pinacol rearrangements reported in this work. Also consistent with this mechanism are the structural requirements of the alcohols which undergo dehydration, namely, benzylic or tertiary alcohols. Therefore, dimethyl sulfoxide appears to serve as a solvent for promoting ionization of alcohols.

In order to determine whether such solvent properties as dielectric constant and dipole moment are mainly responsible for the dehydration of alcohols in dimethyl sulfoxide, a series of high boiling solvents was investigated. When 1-phenyl-1-propanol was heated in these materials at 160° for 14 hr., only starting alcohol was recovered in yields of 82% or better. Table V summarizes these data and clearly shows that, of the examples studied, dimethyl sulfoxide is unique in promoting dehydration. A sample of 2-methyl-2-hexanol was heated in pyridine N-oxide (μ = 4.9[9]) and gave 12% olefin and 65% unchanged alcohol. This amount of olefin could be attributed to a thermal dehydration.[3] Thus the dehydration of alcohols in dimethyl sulfoxide is not a result of the high dielectric strength of this solvent. One must consider other solvating properties.

TABLE V

EFFECTS OF VARIOUS SOLVENTS ON 1-PHENYL-1-PROPANOL AT 160°

Solvent	Dielectric constant,[a] E	Dipole moment,[b] μ	Recovered alcohol, %
Dimethyl sulfone		4.4	90
Acetamide	59	3.7	100
Dimethyl sulfoxide	48.9[c]	3.95	3
Nitrobenzene	36	3.98	82
Benzonitrile	25	3.94	85
Quinoline	9	2.25	93
Diphenylmethane	2.7	2.95	91

[a] A. A. Maryott and E. R. Smith, National Bureau of Standards Circular, No. 514, 1951. [b] L. G. Wesson, "Table of Electric Dipole Moments," The Technology Press, Cambridge, Mass., 1948. [c] H. L. Schlafer and W. Schaffernicht, *Angew. Chem.*, **72**, 618 (1960).

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(7) See A. P. Dunlop and F. N. Peters, "The Furans," Reinhold Publishing Corp., New York, N. Y., 1953, for synthesis of furans.

(8) V. J. Traynelis and W. L. Hergenrother, *J. Org. Chem.*, **29**, 221 (1964).

(9) E. P. Linton, *J. Am. Chem. Soc.*, **62**, 1945 (1940).

Experimental[10]

Dimethyl Sulfoxide.—Dimethyl sulfoxide,[11] b.p. 83° (17 mm.), n^{20}_{D} 1.4795, was purified as previously described.[3]

Starting Materials.—The following available liquids were distilled prior to use and had boiling points corresponding to literature values: 1-phenyl-1-propanol,[3] 5-butyl-5-nonanol, 1,3-butanediol, 2-methyl-2,4-pentanediol, aldol, diacetone alcohol, α-phenethyl ether, and acetonylacetone. The following available solids were recrystallized to literature melting points when necessary: 1,2-diphenylethanol, 1,6-hexanediol, 1-phenyl-1,2-ethanediol, pinacol, and bicyclohexyl-1,1′-diol.[12]

1-Phenyl-2-propanol.—Phenylacetone (50.0 g., 0.372 mole) in 95% ethanol (100 ml.) was added dropwise and with stirring to a solution of sodium borohydride (4.7 g., 0.13 mole) in 95% ethanol (200 ml.) kept at 0.5°. The mixture was refluxed 1 hr., cooled, treated with 10% hydrochloric acid, and extracted with petroleum ether (b.p. 30–60°). The extract was dried and distillation gave 27.0 g. (53%) of pure 1-phenyl-2-propanol, b.p. 103–104° (14 mm.), n^{20}_{D} 1.5200 [lit.[13] b.p. 101–102° (11 mm.), $n^{14.5}_{\mathrm{D}}$ 1.5243].

2-Methyl-2-hexanol, b.p. 137–139°, n^{20}_{D} 1.4183 (lit.[14] b.p. 143°, lit.[15] n^{20}_{D} 1.4186), was prepared in 72% yield by the procedure of Church, Whitmore, and McGraw.[15]

1-Methylcyclopentanol, b.p. 54–56° (25 mm.), m.p. 35–36° [lit.[16] b.p. 135.6 (760 mm.), m.p. 36°], was prepared in 22% yield according to the procedure of Chavanne and Vogel.[16]

1-Alkylcyclohexanols and 2-Cyclohexyl-2-propanol.—1-Methylcyclohexanol, b.p. 55–56° (10 mm.), m.p. 24–25°, n^{20}_{D} 1.4605 [lit.[17] b.p. 55–56° (10 mm.), m.p. 24–25°, n^{20}_{D} 1.4587]; 1-ethylcyclohexanol, b.p. 79° (22 mm.), m.p. 29–30°, n^{20}_{D} 1.4633 [lit.[17] b.p. 78° (20 mm.), m.p. 33°, n^{20}_{D} 1.4642]; 1-isopropylcyclohexanol, b.p. 81.0–81.5° (20 mm.), n^{20}_{D} 1.4682 [lit.[17] b.p. 76–78° (18 mm.), n^{20}_{D} 1.4683]; and 2-cyclohexyl-2-propanol, b.p. 97° (18 mm.), n^{20}_{D} 1.4690 [lit.[17] b.p. 96° (20 mm.), n^{20}_{D} 1.4700], were prepared by reaction of methyl, ethyl, isopropyl, and cyclohexyl Grignard reagents upon the appropriate ketone according to the procedure of Mosher[17] in 76, 55, 38, and 42% yield, respectively.

2,3-Diphenyl-2,3-butanediol.—A mixture of the *meso-* and *dl*-2,3-diphenyl-2,3-butanediol, m.p. 82–112° (lit.[18] m.p. 82–112°), was prepared in 56% yield from acetophenone (47.7 g., 0.397 mole) according to the procedure of Newman.[18]

***dl*-2,3-Diphenyl-2,3-butanediol.**—Pure *dl*-2,3-diphenyl-2,3-butanediol, m.p. 121–122° (lit.[6] m.p. 122°), was obtained from a mixture of the *meso* and *dl* diol by incomplete dehydration in dimethyl sulfoxide. The procedure is described in the section on dehydration of alcohols.

***meso*-2,3-Diphenyl-2,3-butanediol.**—Chromatography of 2.00 g. (0.0082 mole) of 2,3-diphenyl-2,3-butanediol (*meso* and *dl*) on 200 g. of Alcoa F-20 activated alumina gave, upon elution with 1000 ml. of 60% ether in petroleum ether (b.p. 30–60°), 0.30 g. (15%) of pure *meso*-2,3-diphenyl-2,3-butanediol, m.p. 118–118.5° (lit.[6] m.p. 117–118°), and 1.65 g. of a mixture of *meso* and *dl* diol, m.p. 92–114°. A mixture melting point of pure *dl* and pure *meso* was 92–110°.

An alternate method utilized the procedure of Tiffeneau and Levy[19] which involved the addition of phenylmagnesium bromide to biacetyl. A reaction employing 0.10 mole of biacetyl produced pure *meso* diol, m.p. 115.5–117°, in 15% yield and a mixture of *meso* and *dl* diol, m.p. 82–112°, in 30% yield.

1,4-Diphenyl-1,4-butanedione.—Employing the procedure of Conant and Cutter,[20] a solution of sodium hydrosulfite (19.2 g., 0.110 mole) in 100 ml. of water was added to a hot solution of 1,4-diphenyl-2-butene-1,4-dione (23.6 g., 0.100 mole) in 300 ml. of 95% ethanol. After addition was complete, the solution was cooled, poured into water, and the resulting solid collected. Recrystallization from 95% ethanol gave 15.2 g. (64%) of 1,4-diphenyl-1,4-butanedione, m.p. 143–144° (lit.[21] m.p. 144–145°).

Dehydration of Alcohols. General Procedure.[3] Method A.—A solution of alcohol and dimethyl sulfoxide was heated in an oil bath at 160–190° (reflux) under a reflux condenser for the specified periods of time, cooled, and diluted with water. The mixture was extracted with petroleum ether (b.p. 30–60°) and after the extract was dried, the products were isolated and purified by distillation, crystallization, or column chromatography.

Method B.[3]—This varies from the procedure A in that the reflux condenser was replaced by a Claisen head and the product (having b.p.<100°), which distilled during the reaction, was collected in an appropriate receiver cooled in an ice bath or an acetone–Dry Ice bath.

1-Phenyl-2-propanol.—Dry nitrogen was passed through a solution of 1-phenyl-2-propanol (1.3 g., 0.010 mole) and dimethyl sulfoxide (5.5 g., 0.070 mole) for 8 hr. at room temperature and the resulting oxygen-free solution was heated under nitrogen at 190° for 48 hr. The reaction was processed according to method A and analysis of the product by v.p.c. (10-ft. column of Tide detergent on firebrick, at 160°, and a helium flow rate of 60 cc./min.) showed 41% 1-phenylpropene, 48% 1-phenyl-1-propanol, and less than 1% phenylacetone.

1-Methylcyclopentanol.—A solution of 1-methylcyclopentanol (4.00 g., 0.040 mole) and dimethyl sulfoxide (22.0 g., 0.280 mole) was heated at 160° for 6 hr. and processed according to method B. V.p.c. (10-ft. column, Ucon polar on firebrick (30–60 mesh), at 22°, and a helium flow rate of 60 cc./min.) showed only one peak.[22] Distillation of this material gave 2.90 g. (88%) of pure 1-methylcyclopentene, b.p. 74°, n^{20}_{D} 1.4321 (lit.[23] b.p. 75.5–76°, n^{15}_{D} 1.4347).

1-Methylcyclohexanol.—After a solution of 1-methylcyclohexanol (12.50 g., 0.110 mole) and dimethyl sulfoxide (60.0 g., 0.768 mole) was heated at 180° for 9 hr., the reaction mixture was dried over anhydrous sodium sulfate. Distillation gave 8.03 g. (74.5%) of 1-methylcyclohexene, b.p. 52° (110 mm.), n^{20}_{D} 1.4502 [lit.[17] b.p. 110° (760 mm.), n^{20}_{D} 1.4508]. Analysis of this material by v.p.c. (same column as the preceding experiment at 80° and a helium flow rate of 18 cc./min.) showed the presence of 5% of methylene cyclohexane.

A sample of 1-methylcyclohexanol also was dehydrated by distillation from iodine according to the procedure of Mosher.[17] The yield of olefins was 60% with a composition of 95% 1-methylcyclohexene and 5% methylene cyclohexane.

Dehydration of 1-methylcyclohexanol by *p*-toluenesulfonic acid was accomplished by heating these materials in tetralin and distillating out the olefin as formed. Redistillation of this material gave a 37% yield of olefins composed of 97% 1-methylcyclohexene and 3% methylenecyclohexane.

When pure 1-methylcyclohexanol was heated at 180° for 9 hr., no olefins were obtained.

1-Ethylcyclohexanol.—According to method A, 1-ethylcyclohexanol (8.60 g., 0.0651 mole) and dimethyl sulfoxide (35.6 g., 0.456 mole) at 180° for 9 hr. gave 4.0 g. (56%) of 1-ethylcyclohexene, b.p. 61° (79 mm.), n^{20}_{D} 1.4581 [lit.[17] b.p. 134° (760 mm.), n^{20}_{D} 1.4577], and the product was shown by v.p.c. to contain 94% 1-ethylcyclohexene and 6% ethylidenecyclohexane.

When pure 1-ethylcyclohexanol was heated at 180° for 9 hr., an 18% yield of olefin, b.p. 61° (80 mm.), was isolated.

1-Isopropylcyclohexanol.—A solution of 1-isopropylcyclohexanol (2.40 g., 0.019 mole) and dimethyl sulfoxide (10.0 g., 0.128 mole) was heated for 14 hr. at 185° and processed according to method A, giving 1.3 g. (62%) of olefins. V.p.c. (Ucon polar column at 95° and a helium flow rate of 60 cc./min.) showed the presence of 78.3% 1-isopropylcyclohexene, 5.4% 2-cyclohexylpropene, and 16.3% isopropylidenecyclohexane. The first and last compounds listed were separated by v.p.c. and were identi-

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(10) All melting points and boiling points are uncorrected. V.p.c. was performed on Wilkens Aerograph instruments, Model A-90 and A-90P, and the relative peak areas were determined with a Keuffel and Esser Co. No. 4242 compensating planimeter. Infrared spectra were recorded on a Perkin-Elmer Infracord, while the n.m.r. spectra were measured by Mr. B. Nowak and Mr. R. Daignault on a Varian Associates 60-Mc. high resolution n.m.r. spectrometer, Model V-4300B.

(11) The authors wish to thank the Chemical Products Division of the Crown Zellerbach Co. for making generous samples of this material available for this work.

(12) This compound was provided by Professor B. T. Gillis of Duquesne University for which the authors express grateful acknowledgment.

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(17) W. A. Mosher, *J. Am. Chem. Soc.*, **62**, 552 (1940).

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(21) S. Kapf. and C. Paal, *Ber.*, **21**, 3056 (1888).

(22) Although this column was successful in separating the exo- and endocyclic olefins in the cyclohexane system, it may not have been successful in the cyclopentane system and the product may contain some methylenecyclopentane.

(23) G. Chavanne and P. Becker, *Bull. soc. chim. Belges*, **36**, 591 (1927).

fied by their infrared and n.m.r. spectra.[24] In the n.m.r. spectrum, 1-isopropylcyclohexene had a doublet at 9.04 with a weight of 6 protons, a multiplet at 8.20 with a weight of 9 protons, and a singlet at 4.60 τ with a weight of 1 proton, while isopropylidene cyclohexane had two singlet absorptions at 8.53 with a weight of 6 protons and 8.38 τ with a weight of 10 protons. 2-Cyclohexylpropene had the same retention time as the material identified in the following experiment.

2-Cyclohexyl-2-propanol (3.25 g., 0.0227 mole) and dimethyl sulfoxide (12.5 g., 0.160 mole) were heated at 175° for 15 hr., and processed according to method A to give 1.60 g. (57%) of olefins. When this mixture was analyzed by v.p.c., the composition was 72.8% 2-cyclohexylpropene and 27.2% isopropylidene cyclohexane. The 2-cyclohexylpropene was collected from v.p.c. (conditions as before), n^{20}_{D} 1.4575 (lit.[17] n^{20}_{D} 1.4586), and was characterized by its infrared spectrum.

1,2-Diphenylethanol.—A solution of 1,2-diphenylethanol (1.00 g., 0.0050 mole) and dimethyl sulfoxide (3.12 g., 0.040 mole) was heated at 160° for 9 hr. and processed by method A to give 0.90 g. of solid material. Chromatography of this mixture on 80.0 g. of Alcoa F-20 activated alumina and elution with petroleum ether (b.p. 30–60°) gave 0.85 g. (93%) of *trans*-stilbene, m.p. 122–124° (lit.[25] m.p. 125°). Elution with ether gave 0.05 g. (5%) of starting alcohol, melting point and mixture melting point with an authentic sample 64–66°.

1-Phenyl-1-propanol.—Four experiments were performed using 1-phenyl-1-propanol (5.0 g., 0.037 mole) and varying amounts of dimethyl sulfoxide at 175° for 9 hr. The reactions were processed according to method A and gave 4.44, 4.52, 4.80, and 4.75 g. of residue, respectively. The residue composition was determined by v.p.c. (conditions same as described under 1-phenyl-2-propanol). The results of this study appear in Table II.

1,4-Butanediol.—A solution of 1,4-butanediol (36.0 g., 0.400 mole) and dimethyl sulfoxide (15.6 g., 0.200 mole) was heated for 14 hr. at 190° and processed according to method B to give 20.2 g. (70%) of tetrahydrofuran, b.p. 64–65°, n^{20}_{D} 1.4038 (lit.[26] b.p. 64–66°, n^{25}_{D} 1.4040).

1,5-Pentanediol (31.2 g., 0.300 mole) and dimethyl sulfoxide (23.4 g., 0.300 mole) were heated for 24 hr. at 190° and processed according to method B. Fractional distillation of the condensate (24.7 g.) which contained tetrahydropyran, dimethyl sulfide, dimethyl disulfide, and bismethylthiomethane gave 12 g. (47%) of tetrahydropyran, b.p. 87–89°, n^{20}_{D} 1.4255 (lit.,[27] b.p. 88°, n^{20}_{D} 1.4205). This was contaminated with a small amount of by-products containing sulfur and when a pure sample, n^{20}_{D} 1.4208, was collected from v.p.c. its infrared spectrum was identical with that of an authentic sample.

Employing the procedure of Franke, *et al.*,[28] 1,5-pentanediol (10.4 g., 0.10 mole) and 50% sulfuric acid (100 ml.) were heated until tetrahydropyran ceased to distil. Redistillation gave 6.5 g. (76%) of tetrahydropyran, b.p. 86–88°, n^{20}_{D} 1.4190.

1,6-Hexanediol—When a solution of 1,6-hexanediol (23.6 g. 0.200 mole) and dimethyl sulfoxide (7.8 g., 0.100 mole) was heated at 190° for 24 hr. according to method B, 9.5 g. of liquid was collected. Distillation of this condensate gave 4.7 g. (24%) of oxepane, b.p. 116°, n^{20}_{D} 1.4547 (lit.[27] b.p. 116°, n^{20}_{D} 1.4355). A pure sample, n^{20}_{D} 1.4393, was collected by v.p.c. and had an infrared spectrum identical with that of an authentic sample.

Dehydration of 1,6-hexanediol (6.4 g., 0.050 mole) also was accomplished by the method of Franke, *et al.*,[28] and gave 3.0 g. of distillate from which a sample of oxepane, n^{20}_{D} 1.4387, was isolated by v.p.c.

1-Phenyl-1,2-ethanediol.—From 1-phenyl-1,2-ethanediol (13.8 g., 0.100 mole) and dimethyl sulfoxide (54.6 g., 0.700 mole) at 190° for 48 hr., 9.0 g. of a black liquid was obtained by procedure A. A sample (1.00 g.) of this substance was treated with 2,4-dinitrophenylhydrazine and gave 2.0 g. of phenylacetaldehyde 2,4-dinitrophenylhydrazone, m.p. 119–120.5° (lit.[29] m.p. 121°). Based on this analysis the yield of phenylacetaldehyde in the dehydration reaction was 67%.

2-Methyl-2,3-butanediol.—A solution of 2-methyl-2,3-butanediol (15.6 g., 0.150 mole) and dimethyl sulfoxide (93.4 g., 1.20 mole) was heated for 36 hr. at 190° and processed according to method B. Distillation of the condensate gave 8.5 g. (66%) of 3-methyl-2-butanone, b.p. 92–96°, n^{20}_{D} 1.3968, 2,4-dinitrophenylhydrazone derivative m.p. 118–119°, and semicarbazone derivative m.p. 110–112° (lit.[30] b.p. 93°, n^{20}_{D} 1.3879, 2,4-dinitrophenylhydrazone derivative m.p. 117°, semicarbazone derivative m.p. 113°).

2,3-Diphenyl-2,3-butanediol.—Using method A, 2,3-diphenyl-2,3-butanediol (2.0 g., 0.0082 mole) and dimethyl sulfoxide (9.0 g., 0.116 mole) after 14 hr. at 190° gave 1.8 g. of a yellow oil which upon chromatography on 100 g. of Alcoa F-20 activated alumina was separated into 0.30 g. (17%) of 2,3-diphenylbutadiene, m.p. 44–46° (lit.[31] m.p. 49°), which exhibited strong absorption at 11.05 μ in the infrared spectrum, and 1.20 g. (65%) of a mixture of ketones. The ketone mixture was analyzed by v.p.c. (silicone QF-1 column at 220° and a helium flow rate of 40 cc./min.) and contained 11% 1,2-diphenyl-2-methyl-1-propanone and 89% 3,3-diphenyl-2-butanone.

A second experiment was performed using twice the quantities of reactants at 190° for 7 hr. and gave, upon chromatography, 0.50 g. (15%) of 2,3-diphenylbutadiene, 1.20 g. (33%) of a ketone mixture (composition, 19% 1,2-diphenyl-2-methyl-1-propanone and 81% 3,3-diphenyl-2-butanone), and 1.90 g. (48%) of unreacted diol from which 1.3 g. (33%) of pure *dl*-2,3-diphenyl-2,3-butanediol, m.p. 121–122°, was obtained by recrystallization from petroleum ether (b.p. 30–60°).

A sample of the previous ketone mixture (0.50 g.) was treated with sodium hypoiodite in dioxane and gave 0.10 g. (20%) of a brown oil with one carbonyl absorption in the infrared spectrum at 5.95 μ. This was converted to the oxime of 1,2-diphenyl-2-methyl-1-propanone, m.p. 190–192° (lit.[6] m.p. 192–193°).

When pure *dl*-2,3-diphenyl-2,3-butanediol (1.0 g., 0.0041 mole) and dimethyl sulfoxide (4.5 g., 0.058 mole) were heated for 14 hr. at 190° and similarly processed, 0.10 g. (12%) of 2,3-diphenylbutadiene and 0.60 g. (65%) of a ketone mixture were isolated. The ketone mixture was composed of 2% 1,2-diphenyl-2-methyl-1-propanone and 98% 3,3-diphenyl-2-butanone. The oxime of 3,3-diphenyl-2-butanone, m.p. 149–150° (lit.[19] m.p. 151°), was prepared in the usual manner.

A second reaction identical with the preceding experiment except using the *meso* diol and reaction time of 7 hr. gave a 15% yield of 2,3-diphenylbutadiene and a 68% yield of ketones (2.4% 1,2-diphenyl-2-methyl-1-propanone and 97.6% 3,3-diphenyl-2-butanone).

Pinacol.—Anhydrous pinacol, m.p. 35–37° (11.8 g., 0.10 mole) and dimethyl sulfoxide (54.6 g., 0.70 mole) were heated at 160°, 175°, and 185° for 16 hr. and processed according to method B. The condensates were analyzed by v.p.c. (mineral oil column at 75° and a helium flow rate of 40 cc./min.) and contained 52%, 56%, and 55% 2,3-dimethylbutadiene and 20%, 27%, and 30% of pinacolone, respectively. Distillation gave pure 2,3-dimethylbutadiene, b.p. 68–69°, $n^{21.4}_{\mathrm{D}}$ 1.4370; 4,5-dimethyl-1,2,3,6-tetrahydrophthalic anhydride, m.p. 76–78°, lit.[32] b.p. 69–70°, n^{20}_{D} 1.4377 (lit.[33] m.p. 78°); and pinacolone, b.p. 104–105°, n^{20}_{D} 1.3970, 2,4-dinitrophenylhydrazone derivative m.p. 124–125° (lit.[33] b.p. 105°, n^{20}_{D} 1.3956, 2,4-dinitrophenylhydrazone derivative m.p. 126–127°).

When pinacol was heated without dimethyl sulfoxide for 16 hr. at 185°, no product collected in the cold trap and pinacol was recovered quantitatively.

Bicyclohexyl-1,1′-diol.—A solution of bicyclohexyl-1,1′-diol (5.0 g., 0.025 mole) and dimethyl sulfoxide (16.4 g., 0.210 mole) was heated at 160° for 16 hr. and processed according to method A. The resulting yellow oil (4.0 g.) was chromatographed on 150 g. of Alcoa F-20 activated alumina and gave 3.4 g. (85%) of bicyclohexyl-1,1′-diene, n^{20}_{D} 1.5282 (lit.[34] n^{20}_{D} 1.5287) (eluted with petroleum ether), and 0.60 g. of a mixture (eluted with ether) from which was prepared spiro[5.6]dodecan-7-one semicarbazone, m.p. 206–208°, and 2,4-dinitrophenylhydrazone, m.p. 111–113° (lit.[35] semicarbazone m.p. 208–209°, lit.[36] 2,4-dinitrophenylhydrazone m.p. 114°). The diene was characterized by its infrared spectrum and by a Diels–Alder reaction with maleic an-

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[24] The n.m.r. spectra were measured in a carbon tetrachloride solution with tetramethylsilane as an internal standard.

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hydride which gave $\Delta^{12,13}$-dodecahydrophenanthrene-9,10-dicarboxylic acid, m.p. 241–242° (lit.[37] m.p. 242°).

An authentic sample of bicyclohexyl-1,1′-diene was prepared by the procedure of Greidinger and Ginsburg[38] which required the dehydration of bicyclohexyl-1,1′-diol with phosphorus oxychloride in pyridine.

The reaction of bicyclohexyl-1,1′-diol with 50% sulfuric acid by the procedure of Walter[35] gave 79% yield of bicyclohexyl-1,1′-diene and 17% spiro[5.6]dodecan-7-one.

2-Methyl-2,4-pentanediol.—The distillate (16.5 g.), which was collected from 2-methyl-2,4-pentanediol (23.6 g., 0.20 mole) and dimethyl sulfoxide (110 g., 1.40 moles) at 190° for 24 hr. using method B, upon fractional distillation gave 8.0 g. (49%) of a mixture of 2-methyl-1,3-pentadiene and 2-methyl-2,4-pentadiene, b.p. 74–76°, $n^{20}{}_{\rm D}$ 1.4480 (lit.[39] 2-methyl-1,3-pentadiene b.p. 75.6–76.0°, $n^{20}{}_{\rm D}$ 1.4466; 2-methyl-2,4-pentadiene b.p. 76–76.5°, $n^{20}{}_{\rm D}$ 1.45317), and 5.0 g. (25%) of 2-methyl-1-penten-4-ol, b.p. 129–131°, $n^{20}{}_{\rm D}$ 1.4334 (lit.[40] b.p. 130.3°, lit.[41] $n^{20}{}_{\rm D}$ 1.4330).

2-Methyl-1-penten-4-ol.—After a solution of 2-methyl-1-penten-4-ol (4.5 g., 0.045 mole) and dimethyl sulfoxide (24.6 g., 0.318 mole) was heated at 190° for 24 hr. under a reflux condenser, distillation of the reaction mixture gave 2.0 g. (55%) of a mixture of 2-methyl-1,3-pentadiene and 2-methyl-2,4-pentadiene, b.p. 74–76°, $n^{20}{}_{\rm D}$ 1.4472.

1,3-Butanediol.—When 1,3-butanediol (18.1 g., 0.20 mole) and dimethyl sulfoxide (124.8 g., 1.60 mole) were heated for 48 hr. at 190°, 28.7 g. of an organic liquid was collected from the reaction. Distillation of this material gave 4.15 g. (26%) of crotonaldehyde, b.p. 103–110°, $n^{20}{}_{\rm D}$ 1.4403, 2,4-dinitrophenylhydrazone derivative melting point and mixture melting point with an authentic sample 187–189° (lit.[42] b.p. 104–105°, $n^{20}{}_{\rm D}$ 1.4384, lit.[29] 2,4-dinitrophenylhydrazone derivative m.p. 189°), and 8.6 g. (54%) of 2-buten-1-ol, b.p. 112–115°, $n^{20}{}_{\rm D}$ 1.4223 (lit.[43] b.p. 118°, $n^{20}{}_{\rm D}$ 1.4240).

Aldol.—When a solution of aldol (17.6 g., 0.20 mole) and dimethyl sulfoxide (109 g., 1.40 mole) was heated at 190° for 6 hr. and processed according to method B, 10 g. of an organic liquid was obtained. Distillation gave 8.9 g. (64%) of crotonaldehyde, b.p. 103–105°, $n^{20}{}_{\rm D}$ 1.4372, 2,4-dinitrophenylhydrazone m.p. 187–188°.

Diacetone Alcohol.—A solution of diacetone alcohol (12.2 g., 0.10 mole) and dimethyl sulfoxide (54.6 g., 0.700 mole) was heated at 190° for 8 hr. The solution was distilled collecting all material boiling below 150°. Redistillation gave 8.2 g. (81%) of mesityl oxide, b.p. 130–135°, $n^{20}{}_{\rm D}$ 1.4458, 2,4-dinitrophenylhydrazone derivative melting point and mixture melting point with an authentic sample 198–200° (lit.[44] b.p. 131°, $n^{13}{}_{\rm D}$ 1.4484, lit.[29] 2,4-dinitrophenylhydrazone derivative m.p. 203°).

4-Methoxy-4-methyl-2-pentanone.—The reaction of 4-methoxy-4-methyl-2-pentanone (26.0 g., 0.20 mole) and dimethyl sulfoxide (125 g., 1.60 mole) at 190° for 48 hr., gave 10.4 g. of condensate. Distillation of this material gave 5.2 g. (81%) of methanol, b.p. 66–70°, $n^{20}{}_{\rm D}$ 1.3343 (lit.[45] b.p. 64–65°, $n^{20}{}_{\rm D}$ 1.3312), α-naphthylurethane m.p. 118–121° (lit.[46] m.p. 124°). The residue (5.2 g.) from this distillation was combined with 18.4 g. of material, b.p. 140–160°, obtained from distillation of the dimethyl sulfoxide solution. Redistillation of this material gave 17.7 g. (90%) of mesityl oxide, b.p. 128–145°, $n^{20}{}_{\rm D}$ 1.4455, 2,4-dinitrophenylhydrazone derivative m.p. 198–200°.

α-Phenethyl Ether.—After α-phenethyl ether (10.0 g., 0.0442 mole) and dimethyl sulfoxide (24.2 g., 0.31 mole) were heated for 9 hr. at 175°, the reaction was processed according to method A using benzene as the extracting solvent. When the benzene extract was poured into methanol, 3.1 g. (35%) of polystyrene was isolated. An additional 0.4 g. (3%) was isolated upon concentration of the mother liquors.

2,5-Hexanedione.—A solution of 2,5-hexanedione (11.4 g., 0.100 mole) and dimethyl sulfoxide (54.5 g., 0.700 mole) was heated for 60 hr. at 190° and gave 16.1 g. of distillate isolated by method B. Redistillation of this material gave 6.3 g. (66%) of 2,5-dimethylfuran contaminated with dimethyl disulfide, b.p. 94–97°, $n^{20}{}_{\rm D}$ 1.4568 (lit.[47] b.p. 94°, $n^{17.7}{}_{\rm D}$ 1.4427). A pure sample of 2,5-dimethylfuran, $n^{20}{}_{\rm D}$ 1.4403, was collected by v.p.c.

1,4-Diphenyl-1,4-butanedione.—After a solution of 1,4-diphenyl-1,4-butanedione (8.0 g., 0.034 mole) and dimethyl sulfoxide (19 g., 0.24 mole) was heated for 48 hr. at 190° and processed by method A, chromatography of the product on 150 g. of Alcoa F-20 activated alumina gave upon elution with 20% benzene in petroleum ether (b.p. 30–60°), 4.5 g. (60%) of 2,5-diphenylfuran, m.p. 88–89° (lit.[48] m.p. 89.5–90°).

Effect of Base on the Dehydration of Alcohols in Dimethyl Sulfoxide.—Solutions of 5-butyl-5-nonanol, dimethyl sulfoxide, and aniline or sodium *n*-octoxide were heated for 16 hr. at 185° and processed according to method A. Table IV contains a listing of the quantity of reactants and the yield of products. Analysis was accomplished by v.p.c. (Ucon polar column, at 180°, and a helium flow rate of 50 cc./min.).

Similar experiments were performed with 2-methyl-2-hexanol and processed by method A.

In both series the olefins were freed of starting materials and other contaminants by chromatography on alumina.

Attempted Dehydrations of 1-Phenyl-1-propanol in Various Solvents.—A solution of 1-phenyl-1-propanol (0.005 mole) and 0.035 mole of dimethyl sulfone, acetamide, nitrobenzene, benzonitrile, quinoline, or diphenylmethane was heated at 160° for 14 hr. and processed according to method A. The resulting residues from this work-up were examined by v.p.c. and infrared spectra. In some cases the residues were distilled or chromatographed on alumina. No evidence for olefins was found and the recovery of 1-phenyl-1-propanol ranged from 82–100%, see Table V.

Dehydration of 2-Methyl-2-hexanol in Pyridine N-Oxide.—A solution of 2-methyl-2-hexanol (7.20 g., 0.062 mole) and pyridine N-oxide (23.8 g., 0.250 mole) was heated at 185° for 24 hr. and gave 0.60 g. (12%) of the 2-ethyl-1- and 2-hexenes. From the reaction vessel 4.7 g. (65%) of 2-methyl-2-hexanol, $n^{20}{}_{\rm D}$ 1.4170 (starting alcohol, $n^{20}{}_{\rm D}$ 1.4183), was isolated and had an infrared spectrum identical with the starting alcohol.

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