pounds are intermediates, and not the products of a side reaction, in equilibrium with the starting or final products, but not directly concerned in the conversion of the ones to the others.

The data here presented indicate the existence of the ketone amine intermediate, but do not settle the question of its structure, or why it should decompose rapidly with respect to diacetone alcohol. In fact, a mechanism which would depend upon the concentrations of the substituted ammonium ion and hydroxide ion would be indistinguishable kinetically from one depending on the concentration of the amine.

The authors wish to thank Professor M. S. Kharasch for his helpful suggestions during the course of this work.

Summary

1. The rate of the dealdolization of diacetone alcohol has been measured in buffered solutions containing methyl-, dimethyl-, trimethyl- and triethylamine, at several buffer concentrations and buffer ratios.

2. While molecular methyl- and dimethylamine catalyze the reaction, molecular trimethylamine and molecular triethylamine are without effect.

3. It is concluded therefore that the aldol condensation is not an example of general base catalysis.

4. The mechanism of the reaction, in the presence and the absence of amines, is discussed.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Cleavage of Diphenyl Ethers by Sodium in Liquid Ammonia. III. 4,4′-Disubstituted Diphenyl Ethers[1]

BY FRED C. WEBER AND FRANK J. SOWA

It has been shown[2] that a solution of sodium in liquid ammonia reacts vigorously and quantitatively with substituted diphenyl ethers. The products formed are substituted benzenes and phenols. The substituted phenols alone were determined experimentally and it was observed that the relative proportions of the two possible cleavage products formed in each reaction vary with the nature of the substituents in the phenyl nucleus. It was pointed out that the electron is probably the effective cleavage reagent, since sodium amide in liquid ammonia does not cleave diphenyl ether, thus eliminating the possibility of the sodium ion being the effective reagent.

The purpose of this investigation was to determine the effect of various substituents on the manner in which 4,4′-disubstituted diphenyl ethers are cleaved by sodium in liquid ammonia, the method having especial merit because one can make a comparison of the effect of two dissimilar groups within the same molecule.

Experimental

A standard method of cleavage of the diphenyl ethers, outlined in the first article of this series,[2] was used throughout this work. The cleavage products were extracted with ether or benzene and then fractionated using an efficient Widmer column.

TABLE I

PHYSICAL PROPERTIES OF THE DIPHENYL ETHERS PREPARED

No.	Compds. $R—C_6H_4—O—C_6H_4—R'$ R	R′	B. p. at indicated press. °C.	Mm.	M. p., °C.
1	*p*-Methyl	*p*′-Methoxy[a]	193–198	22	49–50
2	*p*-Methyl	*p*′-Nitro	223–227	25	65
3	*p*-Methyl	*p*′-Amino	195–199	16	119
4	*p*-Methoxy	*p*′-Nitro	218–222	16	106–7.5
5	*p*-Methoxy	*p*′-Amino	191–192	4	75–6.5
6	*p*-Methoxy	*p*′-Hydroxy[a]	189–193	16	64–5
7	*p*-Methyl	*p*′-*t*-Butyl[a]	174–178	4	*b*

[a] Compounds previously unreported in the literature.

[b] n^{25}_D 1.5488, sp. gr.$_{25}$ 0.9898.

Compounds nos. (2) and (4) were prepared according to the method of Brewster and Groening, "Organic Syntheses," John Wiley and Sons, Inc., New York, Vol. XIV, p. 67; nos. (3) and (5) by reduction of the corresponding nitro compounds employing the method of Suter, THIS JOURNAL, **51**, 2538 (1929); nos. (1), (6) and (7) were prepared using the method described by Sartoretto and Sowa.[2] All of the diphenyl ethers described in this paper were purified by distillation under reduced pressure.

The cleavages of all of the diphenyl ethers studied, with the exception of the 4-methoxy-4′-hydroxydiphenyl ether, require two atom equiva-

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(1) Original manuscript received July 6, 1937. For previous article see Kranzfelder, Verbanc and Sowa, THIS JOURNAL, **59**, 1488 (1937).

(2) Sartoretto and Sowa, *ibid.*, **59**, 603 (1937).

lents of sodium for each mole of diphenyl ether used. The cleavage of the 4-methoxy-4'-hydroxydiphenyl ether was repeated several times and it was found that four atom equivalents of sodium were required to give a permanent blue coloration with each mole of diphenyl ether used. The products from these cleavages were higher boiling than the original diphenyl ether and have not as yet been identified definitely.

In Table II are listed the diphenyl ethers and the mole percentages of the cleavage products formed in each case. For convenience the groups attached to the oxygen are designated as R and R'.

TABLE II

Compounds R—O—R'		Cleavage products as mole %	
R	R'	ROH	R'OH
p-Tolyl	*p'*-Anisyl	21 *p*-Cresol	79 *p'*-Hydroxyanisole
p-Tolyl	*p'*-Aminophenol	......	100 *p'*-Aminophenol
p-Tolyl	*p'*-*t*-Butylphenyl	48 *p*-Cresol	52 *p'*-*t*-Butylphenol
p-Anisyl	*p'*-Aminophenol	8 *p*-Hydroxyanisole	92 *p'*-Aminophenol

Discussion of Experimental Results

From the experimental results it can be inferred that the linkage between the oxygen and the substituted phenyl group is strengthened against cleavage, by sodium in liquid ammonia, due to the presence of the following substituents, listed according to increasing effectiveness in strengthening this bond: *p*-CH_3, *p*-$C(CH_3)_3$, *p*-OCH_3, *p*-NH_2.

The electron has been shown[2] to be the effective reagent causing cleavage. In the 4,4'-disubstituted diphenyl ethers, the proportion of cleavage at the two carbon atoms adjacent to the oxygen bonds varies depending upon the substituents present. The substituents apparently influence the distribution of electrons in the benzene ring. The electron density of one of the carbon atoms, adjacent to the oxygen atom, is increased to a greater extent than the other at the moment of reaction. From the experimental data it has been possible to determine which substituent influences the configuration to the greatest extent. The series *p*-CH_3, *p*-$C(CH_3)_3$, *p*-OCH_3, *p*-NH_2 lists substituents, in the benzene nuclei, in the order of increasing effectiveness, the order of increasing ortho-para directive power being the same.

From the results of this and previous investigations of diphenyl ether cleavages it is possible to prepare a series of relative electronegativity similar to that suggested by Kharasch.[3] In this work the portion of the molecule which forms the phenolic compound is considered the more electronegative since it does not attract the electrons, which cause the cleavage, to as great an extent as the other portion of the molecule. The series of electronegativity for a carbon to oxygen linkage (which is probably different from a series of carbon to metal, or carbon to nitrogen, etc.) may be drawn up as follows, given in the order of decreasing electronegativity: 4-aminophenyl, 2-aminophenyl, 3-aminophenyl, 4-methoxyphenyl, 4-*t*-butylphenyl, 4-methylphenyl, 3-methylphenyl, 2-methylphenyl, phenyl, 3-methoxyphenyl, 2-methoxyphenyl, 3 - carboxyphenyl, 2 - carboxyphenyl, 4-carboxyphenyl.

Summary

1. Disubstituted diphenyl ethers have been cleaved at the carbon to oxygen bond by means of sodium in liquid ammonia.

2. In 4,4'-disubstituted diphenyl ethers the linkage between the oxygen and the phenyl group is strengthened against cleavage by the following groups, listed according to increasing effectiveness: *p*-CH_3, *p*-$C(CH_3)_3$, *p*-OCH_3, *p*-NH_2.

3. A series of relative electronegativity of substituted phenyl groups has been prepared from the results of these and previous diphenyl ether cleavage reactions.

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[3] Kharasch, *J. Chem. Ed.*, **8**, 1703 (1931).