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

The Cleavage of Diphenyl Ethers by Sodium in Liquid Ammonia. II. Meta Substituted Diphenyl Ethers

BY A. L. KRANZFELDER, J. J. VERBANC AND F. J. SOWA

In a previous publication Sartoretto and Sowa[1] evaluated the effects of various substituents in ortho and para substituted diphenyl ethers on the point of cleavage by sodium in a liquid ammonia solution.

The purpose of this investigation was to study the effects of substituents in the meta position upon the cleavage of diphenyl ethers. Furthermore this cleavage was employed to compare the relative effects of the meta and para and also the meta and ortho positions using the same substituents.

Experimental Part

The preparation of the diphenyl ethers was according to standard procedures with the exception of the 3-carboxydiphenyl ether which was obtained by oxidation of 3-methyldiphenyl ether with potassium permanganate. The yields and physical properties of the diphenyl ethers are listed in Table I.

TABLE I

YIELDS AND PHYSICAL PROPERTIES OF DIPHENYL ETHERS

Diphenyl ether	Yield, %	B. p., °C.	Mm.	d^{25}_{25}	n^{25}_{D}
3-Nitro-	42	174	8	1.2557	1.5998
3-Amino-	81	194	10	1.1584	1.6190
3-Methoxy-	25	127	2	1.1319	1.5775
3-Methyl-	42	138	10	1.0681	1.5713
3-Carboxy-	31	M. p. 139°			
2,3-Dimethoxy-	25	152	2	M. p. 48.5°	
3,4-Dimethoxy-	28	174	4	1.1657	1.5758
2,3-Dimethyl-	47	126	8	1.0529	1.5660
3,4-Dimethyl-	43	163	22	1.0493	1.5649

Cleavage of Diphenyl Ethers.—The cleavage of the diphenyl ethers was accomplished by addition of a solution of sodium in liquid ammonia to a well-stirred solution of the diphenyl ether in liquid ammonia as previously described.[1] The cleavage was complete when the characteristic blue color of sodium in liquid ammonia persisted in the solution. In each case exactly two gram atoms of sodium were required for each gram molecule of diphenyl ether used except in the case of the 3-carboxydiphenyl ether which required three atoms of sodium.

After the liquid ammonia had evaporated the residue was hydrolyzed by the careful addition of water and acidified with dilute hydrochloric acid. As a general procedure the mixture was extracted with ether, dried, the ether removed, and the residue distilled through an efficient column. A fraction was collected for analysis which included the phenols formed during cleavage.

In Table II the cleavage products and methods of analysis are listed. For brevity, the groups attached to the ether oxygen are designated as (R) and (R′).

Theoretical Discussion of Experimental Results

With the exception of the *m*-carboxydiphenyl ether, two atom equivalents of sodium are required to cleave the above listed diphenyl ethers. Whereas *p*-carboxydiphenyl ether reacts with approximately five atom equivalents of sodium, and *o*-carboxydiphenyl ether requires approximately four, *m*-carboxydiphenyl ether is cleaved by the addition of three atom equivalents. It is assumed that two atom equivalents are utilized in the actual cleavage, and one is needed to form the sodium salt of the carboxyl group.

The cleavage of the above diphenyl ethers is explained by considering the electronic theories of Ingold,[2] Robinson,[3] *et al.*, which postulate that the influence of various substituents upon the carbon atoms in a phenyl group consists of two factors: an inductive effect (I) and a tautomeric effect (T). By noting to what relative degree these effects are exhibited by the various substituents in the meta position, and combining this information with the results obtained by Sartoretto and Sowa[1] from the ortho and para substituted diphenyl ethers, it is possible to predict the nature of cleavage of *o,m′*- and *m,p′*-disubstituted diphenyl ethers which contain the same substituent in each phenyl group.

Since the electron (or sodium atom) may be considered as a nucleophyllic reagent, it will attach itself more readily to the carbon atom, linked to oxygen, which has the lowest electron density, and weaken this particular linkage toward cleavage. From the nature of the cleavage therefore, we are able to determine the relative electron densities of the two carbon atoms linked to the ether oxygen. In order to predict the cleavages, then, it is necessary to interpret from theory the effects of the substituents upon the electronic configuration of these carbon atoms.

For simplicity, the carbon atom linked to the oxygen of a phenoxy or substituted phenoxy

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[1] Sartoretto and Sowa, THIS JOURNAL, 59, 603 (1937).

[2] (a) Ingold and Ingold, *J. Chem. Soc.*, 1310 (1926); (b) Ingold, *Chem. Rev.*, 15, 225 (1934).

[3] Robinson, and others, *J. Chem. Soc.*, 401 (1926).

TABLE II

CLEAVAGE PRODUCTS OF DIPHENYL ETHERS

Compound ROR′			Cleavage products as mole %	
R	R′	Method of analysis of cleavage products	ROH	R′OH
Phenyl	3-Aminophenyl	Fractional extraction and distillation	28	72
Phenyl	3-Methoxyphenyl	Fractional distillation	53	47
Phenyl	3-Methylphenyl	Indices of refraction	38	62
Phenyl	3-Carboxyphenyl	Physical properties of phenol, m. p. of acid and anilide	64	36
2-Methoxyphenyl	3′-Methoxyphenyl	Fractional distillation	24	76
3-Methoxyphenyl	4′-Methoxyphenyl	Iodometric titration	8	92
2-Methylphenyl	3′-Methylphenyl	Iodometric titration	47	53
3-Methylphenyl	4′-Methylphenyl	Iodometric titration	23	77

group will be designated as the alpha (α) carbon atom in the following discussion.

In the case of *m*-aminodiphenyl ether, according to the theory, the ($-$I) effect of the *m*-amino group tends to produce a deficiency of electrons at the (α) carbon atom of the substituted phenyl group while the tautomeric effect ($+$T), overbalances this inductive effect with the result that the (α) carbon atom of the substituted phenyl group actually has an electron density greater than that of the (α) carbon atom of the unsubstituted phenyl group. The result was that *m*-aminophenol predominated as a cleavage product. The *m*-carboxyl group exhibits the opposite effect by cleavage to give benzoic acid as the main product. The (α) carbon atom of the substituted phenyl group possesses the lower electron density.

In the case of the sodium salt of *p*-carboxydiphenyl ether the tautomeric effect ($-$T) in combination with the inductive effect is so strong that cleavage takes place completely at the (α) carbon atom of the substituted phenyl group. The ($-$T) effect in the sodium salt of *o*-carboxydiphenyl ether was reduced somewhat. The cleavage, however, takes place at the same point as it did in the para derivative but to a slightly less degree. In the case of the meta compound this effect is reduced to a minimum. As a result of these observations based upon experimental results and reasoning of this sort we can arrange the following series as representing the relative strength of the sodium salt of the carboxyl group at the various positions, $p > o > m$.

Due to the fact that it exhibits no tautomeric effect but does possess a ($+$I) effect, the *m*-methyl group increases the electron density at the (α) carbon atom of the substituted phenyl group and causes *p*-cresol to predominate as a cleavage product. Considering the case of *m*,*p*′-substituted diphenyl ether it was noted by analysis of the cleavage products that the electron density is lower at the (α) carbon atom of the meta-substituted phenyl group. This is according to the theory that the meta position is less affected by the ($+$I) effect of the methyl group than is the para position. This result can also be predicted by noting the extent of cleavage of *m*-methyldiphenyl ether and *p*-methyldiphenyl ether. On the other hand, the cleavage of *o*,*m*′-diphenyl ether shows that the methyl group in the meta position exhibits a ($+$T) effect which is greater than that produced by that group in the ortho position. This statement is also in direct accordance with experimental results, since *m*-methyldiphenyl ether cleaves to a greater extent than *o*-methyldiphenyl ether at the linkage between oxygen and the (α) carbon atom of the unsubstituted phenyl group.

The methoxy group exhibits a ($-$I) effect, and a tautomeric effect ($+$T) that is directly opposed to it. As indicated by the cleavage of *m*-methoxydiphenyl ether, the inductive effect of this substituent in the meta position predominates over the tautomeric effect since the latter would tend to build up electron density at the (α) carbon atom of the substituted phenyl group. By a study of the cleavage of *p*-methoxydiphenyl ether it is seen that in the para position the methoxy group exerts a greater tautomeric influence than it does in the meta position. This, together with the fact that the methoxy group in the meta position may exhibit some inductive effect as shown above, gives the (α) carbon atom of the meta-substituted phenyl group in the *m*,*p*′-dimethoxydiphenyl ether a much lower electron density. The results of cleavage agree with this theory.

By comparing the cleavages of *m*-methoxydiphenyl ether and *o*-methoxydiphenyl ether, it is seen that the electron density at the (α) carbon atom of the substituted phenyl group is greater in the case of the former compound. This indicates that in the meta position the methoxy group produces a greater tautomeric effect than it does in the ortho position. The cleavage of *o,m'*-substituted diphenyl ether bears out this statement, since it occurs to a greater extent at the linkage between oxygen and the *o*-substituted phenyl group.

Although the above is an attempt to explain the experimental results on the basis of tautomeric and inductive effects, it is quite obvious that these effects do not deal entirely satisfactorily with ortho substituted compounds.

Summary

Several diphenyl ethers with substituents in the meta position of one of the phenyl groups have been prepared and cleaved quantitatively by sodium in liquid ammonia.

Exactly two gram atoms of sodium were required to cleave one gram molecule of the diphenyl ether except in the case of 3-carboxydiphenyl ether, in which case three gram atoms were required.

The positions arranged according to decreasing effectiveness of the inductive influence of the methyl group are: para, meta, ortho.

The cleavage products of the methoxy group in the meta and ortho position are not explained satisfactorily on the basis of inductive and tautomeric effects alone.

Groups that strengthen the linkage between oxygen and the substituted phenyl group against cleavage, arranged in the order of their increasing effectiveness, are: *o*-CH_3, *m*-CH_3, *m*-NH_2, *p*-CH_3, *p*-OCH_3, *o*-NH_2, and *p*-NH_2.

Groups that weaken the linkage between oxygen and the substituted phenyl group toward cleavage, arranged in the order of their increasing effectiveness, are: *m*-OCH_3, *o*-OCH_3, *m*-CO_2Na, *o*-CO_2Na, and *p*-CO_2Na.

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Sulfonic and Sulfuric Esters as Alkylating Agents in Liquid Ammonia

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Introduction

Alkylation in liquid ammonia was accomplished by Picon,[1] who utilized the reaction of the alkyl iodides upon sodium acetylide to prepare the alkylacetylenes. Vaughn, Vogt and Nieuwland[2] showed that the alkyl bromides could be used with sodium phenoxide and the sodium alkoxides in liquid ammonia under pressures of from one to ten atmospheres to give fair yields of ethers.

Hurd and Meinert[3] substituted methyl and ethyl sulfates for the alkyl iodides in the preparation of methyl- and ethylacetylene, while Heisig[4] and Heisig and Davis[5] have reported that sodium methyl acetylide can be alkylated by either methyl iodide or methyl sulfate in liquid ammonia.

Although various esters other than the alkyl halides have been employed as alkylating agents, the only such reactions that have been carried out in a liquid ammonia medium have involved the use of methyl and ethyl sulfates. The purpose of this investigation, therefore, was to extend the reaction to other alkyl sulfates, and to test the generality of the reaction with *p*-toluenesulfonic, phosphoric and acetic esters.

Experimental Part

Preparation of Esters.—*n*-Propyl *p*-toluenesulfonate,[6] *n*-amyl sulfate,[7] and sodium phenyl sulfate[8] were prepared by methods described in the literature.

Preparation of *n*-Butyl *p*-Toluenesulfonate.—A modification of the above method[6] was used with the result that the yields were increased considerably. To 185 g. (2.5 moles) of *n*-butyl alcohol was added 11.5 g. (0.5 mole) of sodium, which was first granulated by heating in xylene to its melting point (97.5°) and shaking. The sodium was added in small portions and the alcohol heated to melt the metal. The temperature was allowed to drop to 50° and 97 g. (0.5 mole) of *p*-toluenesulfonyl chloride added in small portions with stirring. The mixture was filtered to remove the sodium chloride formed and washed with *n*-butyl alcohol. The excess alcohol was recovered by distillation at temperatures below 60° (12 mm.). The yield of ester amounted to 98 g. (98% of the theoretical), b. p. 170–172° (10 mm.).

Preparation of *n*-Propyl Sulfate.—Cyclopropane was bubbled into one mole of concd. sulfuric acid with vigorous

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(1) Picon and Lebeau, *Compt. rend.*, **156**, 1077 (1913).

(2) Vaughn, Vogt and Nieuwland, THIS JOURNAL, **57**, 510 (1935).

(3) Hurd and Meinert, *ibid.*, **52**, 4540 (1930); **53**, 289 (1931).

(4) Heisig, *ibid.*, **53**, 3245 (1931).

(5) Heisig and Davis, *ibid.*, **57**, 339 (1935).

(6) Gilman, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1932.

(7) Barkenbus and Owen, THIS JOURNAL, **56**, 1204 (1934).

(8) Burkhardt, *J. Chem. Soc.*, 336 (1933).