

ceeded slowly at room temperature, and the blue paramagnetic solution was directly formed after a period of 2 weeks. As soon as enough of the biphenyl anion had been produced to be easily observed by esr the reaction was stopped by removing the solution from the metal.

Use of dilute solutions, mild conditions, and incomplete reaction led to very low yields (<5%). For this reason, no attempt was made to isolate, purify, and identify products by classical procedures. Aliquots of the reaction mixtures were removed at various times from contact with the metal, opened to air, and analyzed by vpc. An Aerograph Model 600-C vapor phase chromatograph was used for the vpc analysis and the column used was 5% SE 30 on Chromosorb W 30-60 mesh (1/8 in.  $\times$  5 ft) at 85-150°. Four distinct peaks were observed in addition to the solvent peak. The order of elution was solvent peak, aniline, biphenyl, diphenylamine and finally triphenylamine. The identities of the peaks were based on comparisons with vpc analyses of known solutions of these compounds both individually and in mixtures.

For the isolated study of reaction 2, Ph<sub>2</sub>NK was prepared from Ph<sub>2</sub>NH and K. The solution was outgassed to eliminate H<sub>2</sub> and the glassware was joined to a second reaction apparatus by means of a break-seal. LiPh was produced in this second apparatus by the reaction of Li with bromobenzene at -30°. The two solutions were then mixed *via* the break-seal, and aliquots were analyzed by vpc.

*p,p',p''*-Trideuteriotriphenylamine was prepared from *p,p',p''*-tribromotriphenylamine. The latter compound was dissolved in a small volume of dry ether contained in a three-neck flask equipped with a reflux condenser, a dry nitrogen inlet, and a serum cap. A solution of *n*-butyllithium (~175% excess) in hexane was added through the serum cap by means of a syringe over a period of 1 hr. The solution was stirred for 1 hr and 99.7% isotopic purity D<sub>2</sub>O (about a 200% excess) was added. The solvent was removed leaving a yellow oil. It was decolorized with Norit and recrystallized from ethanol. The nmr spectrum of the purified material was consistent with the deuteration of the *para* positions of the aromatic rings.

### Cleavage of *o*- and *p*-Biphenyl Phenyl Ethers with Sodium and Liquid Ammonia

E. J. STROJNY

The Benzene Research Laboratory,  
The Dow Chemical Company, Midland, Michigan

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The cleavage of *o*- and *p*-biphenyl phenyl ethers with sodium and liquid ammonia gave biphenyl and phenol as the exclusive cleavage products.<sup>1</sup> This behavior was unexpected in view of the results obtained by other investigators of this reaction.<sup>3-7</sup> Sowa and co-workers<sup>3,4</sup> found that in unsymmetrically substituted phenyl ethers, the phenyl group which had the stronger *ortho-para* directing substituent yielded the greater proportion of phenol on cleavage. In only three compounds did they find exclusive cleavage at one of the two carbon-oxygen bonds. These were *p*-aminophenyl phenyl ether, *p*-aminophenyl *p*-tolyl ether, and *p*-carboxyphenyl phenyl ether. Pirkle and Zabriskie<sup>7</sup>

have taken advantage of the strong directive influence of the amino group in developing a method for replacing aromatic hydroxyl groups with hydrogen.

The biphenyl phenyl ether system has not been studied before. The closest chemically related systems were the cleavage of  $\alpha$ - and  $\beta$ -naphthyl phenyl ethers studied by Tomita, *et al.*<sup>6</sup> They found naphthalene and  $\alpha$ - and  $\beta$ -naphthols in their products, indicative of cleavage taking place at both the naphthyl-oxygen and phenyl-oxygen bonds. Eargle<sup>2</sup> demonstrated by esr that two electrons are transferred from sodium atoms to the ether molecule before cleavage takes place. He also stated that after cleavage occurs these electrons are most likely localized on the aryl rather than the aryloxy fragment. The cleavages of the biphenyl phenyl ethers gave the products which can be predicted by such a mechanism. The biphenyl group, with the greater electron system, would be expected to stabilize the negative charge better than the phenyl group. Therefore, the cleavage would be expected to occur at the biphenyl-oxygen bond. However, as was demonstrated with  $\alpha$ - and  $\beta$ -naphthyl phenyl ethers, exclusive cleavage at a given aryl-oxygen bond cannot be predicted by such reasoning. The exclusive cleavage at the biphenyl-oxygen bond could not have been predicted by Sowa's observations<sup>4</sup> either. On the contrary, since a phenyl group is *ortho-para* directing, the phenylphenols would be predicted as the major phenolic products.

At present, we have no explanation for the apparent conflicting behavior of the naphthyl phenyl and the biphenyl phenyl ethers toward cleavage in sodium-liquid ammonia solutions.

#### Experimental Section

The procedure for the preparation of substituted phenyl ethers, described by Randall, Lewis, and Slagan,<sup>8</sup> was used to prepare *o*- and *p*-biphenyl phenyl ethers. We used *o*- and *p*-potassium phenylphenolates and bromobenzene as the reagents. Gas chromatography showed a single peak for each of the purified ethers.

**Cleavage of *o*-Biphenyl Phenyl Ether.**—To a stirred mixture of 200 ml of liquid ammonia, 100 ml of dry diethyl ether, and 24.63 g (0.100 mole) of *o*-biphenyl phenyl ether was added 4.60 g (0.200 g-atom) of sodium in small pieces over a 2-hr period. After 1 hr of stirring, 75 ml of methanol was slowly added to the red-brown mixture. After evaporation of ammonia, ether (200 ml) and water (100 ml) were added.

An aliquot of the aqueous layer was analyzed for phenol by bromate-bromide titration; 86.5% of theory was found. Acidification of the remaining water solution was followed by extraction twice with ether. The ether extracts were combined, dried, and evaporated to leave a residue which was dissolved in cyclohexane and examined for *o*-phenylphenol by gas chromatography. No *o*-phenylphenol was found.

The ether solution of the neutral material was dried and evaporated to leave 16.31 g of crystals which was dissolved in cyclohexane and analyzed for biphenyl and *o*-biphenyl phenyl ether by gas chromatography. The mixture was found to contain 13.7 g (0.089 mole) of biphenyl and 2.6 g (0.010 mole) of starting material. Material balance was 97-99%.

**Cleavage of *p*-Biphenyl Phenyl Ether.**—In the same manner as above 0.100 mole of *p*-biphenyl phenyl ether was treated with sodium-liquid ammonia. The products were separated into a phenolic and a neutral fraction. Titration for phenol showed 84% of theory was formed. No *p*-phenylphenol was observed by gas chromatography. The neutral fraction contained 12.85 g (0.083 mole) of biphenyl and 3.00 g (0.012 mole) of starting material. Material balance was 94-95%.

(1) Small amounts of aromatic coupling compounds can also form.<sup>2</sup> These are not discussed here.

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