Because these compounds were readily available, it was decided to determine the σ constants by still another procedure. The ionization constants were determined at 25° in 50 vol % aqueous ethanol and compared with that of benzoic acid determined under like conditions. The value for ρ for this ionization is 1.423.[2] The ionization constants found were 5.32, 5.27, and 5.71[3] for the *m*- and *p*-picrylbenzoic and benzoic acids, respectively. σ values calculated from this data are 0.274 for the *m*-picryl group and 0.309 for the *p*-picryl group.

Although these σ values are smaller than those reported previously,[1] they are within the range of differences found for other groups.[2] It is to be noted also, that the ordering of these constants are in the reverse of the earlier values and differ by about 13%.

Experimental Section

The preparation of the *m*- and *p*-picrylbenzoic acids are described elsewhere.[1]

Determination of p*k* Values.—Approximately 0.25 mequiv of the acid was dissolved in 10 ml of absolute ethanol, and 8 ml of water was added and mixed. The solution was titrated potentiometrically with standard sodium hydroxide solution, using a Beckman Model G pH meter. For each aliquot of base added, a volume of water was added so that at the calculated half-neutral point the solution would be 50 vol % ethanol. The equivalent point was determined from which the half-neutral point was found. The pH meter reading was taken as the p*k* value. The pH meter was standardized with aqueous potassium hydrogen phthalate (NBS), and so the actual pH may be different for the organic solvent. However, the σ values were obtained by using the differences in p*k* between benzoic acid and the desired acid, and these differences are probably correct.

A check on the p*k* obtained by the above procedure was obtained by preparing a second solution exactly half-neutralized made up in 50 vol % ethanol. These pH meter readings agreed with those reported above within 0.02 pH unit.

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[3] J. D. Roberts, E. A. McElhill, and R. Armstrong [*J. Am. Chem. Soc.*, **71**, 2923 (1949)] reported that the p*k* for benzoic acid is 5.75 determined by the same procedure.

The Reaction of Triphenylamine with Alkali Metals. Observations on the Mechanism

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Wittenburg and Gilman[3] have shown that triphenyl derivatives of group Vb elements are easily cleaved by alkali metals (M) in tetrahydrofuran (THF), according to the equation

$$\mathrm{Ph_3(Vb)} + 2\mathrm{M} \longrightarrow \mathrm{Ph_2(Vb)M} + \mathrm{MPh}$$

The connection between this general reaction and subsequent free-radical formation has been described for Ph_3P.[4] We now wish to report the results of similar studies on Ph_3N.

Ph_3N was dissolved in THF and reacted with Li, Na, and K, using the customary high-vacuum procedures. The general reaction given above was observed together with formation of the biphenyl negative ion, identified by its well-known electron spin resonance (esr) spectrum.[5] No free radicals were observed by esr prior to the detection of $Ph_2\cdot^-$.

As the reaction proceeded, aliquots were removed, opened to air, and analyzed by vapor phase chromatography. In every case, biphenyl and aniline were obtained in about equal amounts together with small (and variable) amounts of Ph_2NH. (The metal phenide converted to benzene, which was merged with the THF solvent peak). Relatively large amounts of unreacted Ph_3N were also observed. Biphenyl was present in solution prior to subsequent reduction to the corresponding anion radical.

These observations can be explained by the following reaction sequence.

$$\mathrm{Ph_3N} + 2\mathrm{M} \longrightarrow \mathrm{Ph_2NM} + \mathrm{MPh}^{3} \qquad (1)$$

$$\mathrm{Ph_2NM} + \mathrm{MPh} \longrightarrow \mathrm{Ph_2} + \mathrm{PhNM_2} \qquad (2)$$

$$\mathrm{Ph_2} + \mathrm{M} \longrightarrow \mathrm{Ph_2}\cdot^{-} + \mathrm{M}^{+} \qquad (3)$$

$$\mathrm{M} = \mathrm{Li, Na, or\ K}$$

A crucial test of this explanation would be the study of reaction 2, isolated from either reaction 1 or reaction 3. For this test, Ph_2NK was prepared and treated with freshly prepared LiPh. Vapor phase chromatographic analysis showed that biphenyl and aniline were produced in equal amounts, confirming reaction 2, and also indicated the absence of a detectable amount of $PhNH_2$, suggesting that this reaction was quantitative.

If *p,p′,p″*-trideuteriotriphenylamine was used as starting material, the corresponding *p,p′*-dideuteriobiphenyl anion radical was produced, identified by esr. The formation of biphenyl from Ph_3N therefore appears to involve the successive breaking of two carbon–nitrogen bonds, the first cleavage occurring by the reaction with alkali metals and the second cleavage occurring with alkali metal phenides.[6]

Experimental Section

All compounds were purified by recrystallization until literature melting points were obtained and no impurities were detected by vapor phase chromatography (vpc).

Ph_3N (70–120 mg) was dissolved in *ca.* 10 ml of THF in the glass apparatus usually used for esr studies[4] to form solutions ranging from 3–5 × 10^{-2} *M*. After degassing the THF the initial reaction between Ph_3N and either Na or Li was conducted at room temperature; the corresponding reaction with K was usually conducted in the range 0–10°. In the cases of Na or K, after the solutions became yellow-brown due to the initial reaction, they were cooled to −50° and reacted further. The blue color of the biphenyl anion radical was observed at the surface of each metal and confirmed by esr. The reaction of Li with Ph_3N pro-

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[6] The support of the donors of the Petroleum Research Fund is gratefully acknowledged.

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. × 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_2NK was prepared from Ph_2NH and K. The solution was outgassed to eliminate H_2 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 ($\sim$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_2O (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*-Biphenylyl Phenyl Ethers with Sodium and Liquid Ammonia

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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.[1] This behavior was unexpected in view of the results obtained by other investigators of this reaction.[3-7] Sowa and coworkers[3,4] 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[7] have taken advantage of the strong directive influence of the amino group in developing a method for replacing aromatic hydroxyl groups with hydrogen.

The biphenylyl phenyl ether system has not been studied before. The closest chemically related systems were the cleavage of α-and β-naphthyl phenyl ethers studied by Tomita, *et al.*[6] They found naphthalene and α- and β-naphthols in their products, indicative of cleavage taking place at both the naphthyl–oxygen and phenyl–oxygen bonds. Eargle[2] 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 biphenylyl 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 α- and β-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[4] 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 biphenylyl 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,[8] was used to prepare *o*- and *p*-biphenylyl 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*-Biphenylyl 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*-biphenylyl 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*-biphenylyl 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*-biphenylyl 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%.

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[1] Small amounts of aromatic coupling compounds can also form.[2] These are not discussed here.

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