ture and atmospheric pressure[13] until about 0.02 mole of hydrogen had been absorbed. The flask was opened; acetic acid (2 ml)[4] and 1.78 g (0.022 mole) of 37% formalin in 20 ml of absolute ethanol were added; and the reduction was continued until 0.02 additional mole of hydrogen was absorbed. The catalyst was removed by filtration and the ethanol was removed on a rotary evaporator. The thick oil was dissolved in 150 ml of 6 *N* hydrochloric acid, extracted with ether, and allowed to stand overnight. The last traces of ether were removed on a rotary evaporator and the solution was hydrogenated over 2 g of 10% palladium on carbon, again at room temperature and atmospheric pressure. After 0.02 mole of hydrogen had been taken up,[14] the catalyst was removed by filtration and the solution was concentrated to about 20 ml and cooled. Crystals formed and were collected to yield 2.73 g (59.3%) of crude 6-hydroxy-7-methoxy-N-methyl-1,2,3,4-tetrahydroisoquinoline hydrochloride, mp 276–280°. Five recrystallizations from ethanol raised the melting point to 285–290° for the analytical sample.

Anal. Calcd for $C_{11}H_{15}NO_2 \cdot HCl$: C, 57.47; H, 7.02; Cl, 15.43; N, 6.09. Found: C, 57.90; H, 7.11; Cl, 15.44; N, 6.06.

The **free base** was prepared by basification of an aqueous solution of the hydrochloride with ammonia. Two recrystallizations from benzene yielded an analytical sample, mp 164–165°.

Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.36; H, 7.82; N, 7.25. Found: C, 68.23; H, 7.69; N, 7.33.

7-Hydroxy-6-methoxy-N-methyl-1,2,3,4-tetrahydroisoquinoline (5b).—The reactions were carried out exactly as described for **5a** except for the product isolation. The aqueous acid solution was evaporated completely to dryness and dissolved in a minimum amount of water. The solution was made strongly basic (pH 10) with ammonium hydroxide and the product (3.64 g, 94%, mp 166–170°) precipitated. One recrystallization from benzene raised the melting point to 171–173° (lit.[5] mp 168°). A **picrate** melted at 174–177° (lit.[5] mp 178°).

6,7-Methylenedioxy-N-methyl-1,2,3,4-tetrahydroisoquinoline (5c).—The reactions were carried out exactly as described for **5a** except for the product isolation. The aqueous acid solution was evaporated to a small volume and 50 ml of absolute ethanol was added and subsequently evaporated. The alcohol addition was repeated twice more. The product crystallized during this process and was removed by filtration to yield 3.06 g (67%) of **5c** as its hydrochloride, mp 263–269°.[15] The **free base**, mp 60–61.5° (lit. mp 60–61°,[5] 66°[16]), was prepared as described above for **5b**. A **picrate** was prepared from the free base and melted at 175–179° (lit.[16] mp 175–176°).

6,7-Methylenedioxy-N-alkyl-1,2,3,4-tetrahydroisoquinolines (10). General Procedure.—Piperonal (15 g, 0.1 mole) and the appropriate amine (0.1 mole)[17] were dissolved in 50 ml of absolute ethanol and added to a hydrogenation flask containing platinum (from 0.4 g of platinum oxide, prereduced in the flask) and 20 ml of absolute ethanol. The mixture was reduced at room temperature and atmospheric pressure until 0.1 mole of hydrogen had been absorbed. The catalyst was removed by filtration and the residue was taken up in 30 ml of 6 *N* hydrochloric acid and washed with ether. The aqueous solution was made strongly basic with sodium hydroxide (30%) and extracted three times with ether. The ether solution was dried over anhydrous sodium sulfate and evaporated to a residual oil. The oils were not further purified and were not analyzed.

The crude, oily amines (0.015 mole) and glycidol (1.3 g, 0.0175 mole) were mixed in a test tube protected from moisture with a drying tube and heated in a boiling water bath for 2 hr.

The adducts were dissolved in 25 ml of chloroform, added to 25 ml of water, and cooled to 0°. Sodium metaperiodate (3.3 g, 0.015 mole) in 20 ml of water was added dropwise to the stirred, two-phase system. After the addition was complete (15 min), the mixtures were made basic to pH 8 with 1 *N* sodium hydroxide and stirred for 3 hr. The layers were separated and the chloroform layer was extracted with three, 20-ml portions of 6 *N* hydrochloric acid.

The aqueous acid solutions were allowed to stand overnight and reduced over 2.5 g of 5% palladium on carbon until hydrogenation essentially ceased. The catalyst was removed by filtration and the aqueous solutions were evaporated on a rotary evaporator to dryness. The residue was recrystallized from ethanol to give the hydrochlorides listed in Table I in the specified yields and with the specified melting points. Analytical samples were prepared by recrystallization from ethanol.

The nmr spectra of the hydrochlorides listed in Table I were measured in deuterium oxide against tetramethylsilane as an external standard. The spectra showed the predicted peaks for the various N-alkyl residues as well as the following peaks in common: two singlets of one proton each at about τ 3.25 (C-6 and C-8 protons), one singlet of two protons at 4.1 (methylenedioxy), a singlet or doublet of two protons at 5.7 (C-1 protons), and two, broad multiplets of two protons each at 6.3 and 6.8 (C-3 and C-4). When the N-alkyl group was primary (**10**, R = CH_3, CH_3CH_2, and $CH_3CH_2CH_2$) the C-1 protons appeared as a doublet in the spectra. When the N-alkyl group was secondary or tertiary [**10**, R = $(CH_3)_2CH$, and $(CH_3)_3C$] the C-1 protons appeared as a singlet.

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[13] Pressures up to 10 psi were safe, but decomposition sometimes occurred at higher pressure.

[14] The reaction was terminated after 0.02 mole of hydrogen had been absorbed, even though it had not completely stopped.

[15] The melting point of this compound was erratic, sometimes being as high as 300°.

[16] E. Späth and P. L. Julian, *Ber.*, **64**, 1131 (1931).

[17] In the cases of methylamine and ethylamine, these were 8 g of a 40% aqueous solution and 6.5 g of a 70% aqueous solution, respectively. Otherwise, the liquid amines were used.

The Electron Paramagnetic Resonance Detection of Aryl Ether Cleavage. II. The Anion Radicals of Polyphenyl Ethers[1,2]

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The cleavage of the anion radicals of *m*-polyphenyl ethers has been found to produce, initially, the diphenoxide radical of diphenyl ether and biphenyl anion radical.

Metal reduction techniques exercised upon aryl ethers have, in the past, resulted in ready scission.[1,3] The reductive stability of several polyphenyl ethers was investigated in this research to determine if increased stability over simple diaryl ethers might accrue from increased chain length or if possible unusual cleavage reactions might be observed. The compounds investigated and tabulated in Table I produced cleavage products detectable by electron paramagnetic resonance (epr) within seconds; all the fragments were not those which might have been predicted from earlier research. As might be expected from knowledge of the fate of previously studied diaryl ethers, the diether $(Ph)_3O_2$ was found to cleave off both phenyl groups, forming biphenyl and the dipotassium salt of hydro-

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[1] Paper I. Diaryl Ethers: D. H. Eargle, Jr., *J. Org. Chem.*, **28**, 1703 (1963).

[2] Research performed at the U. S. Naval Research Laboratory and presented in part at the 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

[3] E. J. Strojny, *J. Org. Chem.*, **31**, 1662 (1966).

Figure 1.

TABLE I

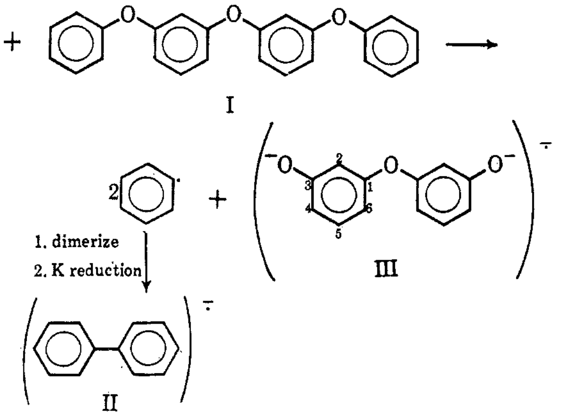
RADICALS OF POLYPHENYL ETHERS

Compd[a]	Linkage	Results
$(Ph)_3O_2$	*para*	Biphenyl negative ion spectrum[b]
$(Ph)_4O_3$[c] (I)	"Mostly *meta*"	Signal $\sim(Ph)_5O_4$, but with some $(PH)_2 \cdot^-$ admixture
$(Ph)_5O_4$	*meta*	Quintet of triplets (four protons split by two protons) $\Delta H = 22.5$ gauss, $a_1 = 4.61$ gauss, $a_2 = 2.09$ gauss[d]
$(Ph)_6O_5$	*meta*	Same as $(Ph)_5O_4$, but with some line broadening

[a] Ph signifies the benzene ring. [b] M. G. Towsend, *J. Chem. Soc.*, 51 (1962). [c] The *meta*-linked ethers were obtained from Dr. Reigh Gunderson as numbered compounds of the Dow-Corning Co. Dr. Gunderson also supplied us with a generous quantity of *p*-diphenoxybenzene $[(Ph)_3O_2]$. [d] Intensity ratios: a_1, 1:4:6:4:1; a_2, 1:2:1.

quinone (undetectable by epr). The ethers with more than two ether linkages also lost their end phenyl groups, but, unexpectedly, one ether linkage was retained in the initial cleavage product.

The epr analysis of the cleavage materials shows that the products of the reaction of potassium with the ethers are the ubiquitous biphenyl negative ion (II) and, initially, the diphenoxide radical of diphenyl ether (III). Since the spectrum of the product III [from $(Ph)_4O_3$] is so well resolved (Figure 1), a comment should be made concerning the structures of the products involved. Without doubt, the species affording the major spectrum is a cleavage product (III) in which the end phenyl groups of the parent ether have been severed. The severed phenyl groups then dimerize with further reduction to biphenyl negative ion. The cleavage product III spectrum results from a primary splitting (4.65 gauss) by the four 4 and 6 protons (*para* to oxygen). Splitting by the two 5 (*meta*) protons was not observed. This interpretation is entirely in line with spectra observed in *meta*-diol radicals.[4]



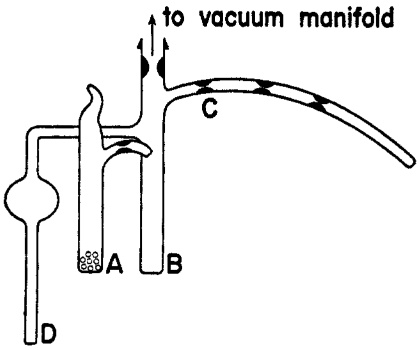


Figure 2.

We must assume that there is a rapid initial reduction of the ethers, followed by an immediate cleavage[1,3] to the observed products. The electron affinity of these ethers must be rather high, owing to the ability of a free electron to conjugate rapidly over the ether linkage.[5] This high affinity is indeed demonstrated by the very rapid reduction (2–3 sec) by potassium of the ethers even at −70°. It now appears possible that highly energetic radicals of a sort formed in thermal and oxidative cleavage reactions might also be trapped by utilizing this high electron affinity. Thus, the ethers may serve as an effective radical trap, reducing the destructive ability of such radicals and affording the well-known stability of such ethers toward oxidative and thermal decomposition.

Summary

We have shown that polyphenyl ethers are readily cleaved by metal reduction techniques, that the cleavage products are readily detectable by epr, and that the cleavage mechanism may be described by an unambiguous series of steps.

Experimental Section

Reduction.—Liquid materials to be treated were distilled, after degassing, under high vacuum from Linde 5A sieves in compartment A of the sample apparatus (Figure 2) into compartment B. After about 25–30 mg of material was obtained, portion A was sealed off. Potassium metal was successively distilled into tube C, while the liquid polymeric material in B was kept cold with an ice bath in order to lower its vapor pressure sufficiently to prevent reaction with the potassium vapor. About 2–3 ml of solvent was then distilled into segment B using liquid nitrogen. When the entire apparatus had been sealed and removed from the vacuum system, it was immersed in a Dry Ice–isopropyl alcohol bath and tilted to allow the solution to come into contact with the metal in the cold. The blue-to-green reduced material was then tipped into the sample tube D and the bulb above it. The filled sample tube was then quickly removed to the precooled (−85°) epr cavity.

Continued reduction or warming to near room temperature resulted in destruction of the epr signal. Presumably, even the radical III decomposed further into diamagnetic materials.

Solvents.—Dimethoxyethane was used in all the experiments reported. Sodium and 2-methyltetrahydrofuran solvent resulted in no spectrum or color whatever with $(Ph)_5O_4$; potassium in 2-methyl tetrahydrofuran gave a color, but not with paramagnetic material, even after 1 week of contact.

Instrument.—All experiments were performed at −50 to −85° on a Varian V-4501A spectrometer, equipped with 100-kc modulation.

Registry No.—I, 748-30-1; $(Ph)_3O_2$, 3061-36-7; $(Ph)_5O_4$, 2455-71-2; $(Ph)_6O_5$, 3705-62-2.

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(4) T. J. Stone and W. A. Waters, *J. Chem. Soc.*, 4302 (1964).

(5) D. H. Eargle, Jr., and S. I. Weissman, *J. Chem. Phys.*, **34**, 1804 (1961).