butylperoxy)hexyne-3 (Lupersol 130) was dissolved in an ether solution of methyl abietate. Isomerization proceeded at the same rate at 200° C. as that of methyl abietate without added inhibitor. After 1 hour at 200° C., 2.3% of methyl dehydroabietate was detected, and after 24 hours at 200° C., the dehydroabietate content was 12%. (B) Cumene hydroperoxide was substituted for Lupersol 130, and essentially the same results were obtained. (C) To a solution prepared as in (A) above was added a methanol solution containing 5 mole % (based on methyl abietate) of potassium hydroxide. No isomerization or disproportionation occurred after heating at 200° C. for 4 days.

Isomerization of Methyl Abietate in the Presence of Abietic Acid at 200° C. A 1-to-1 molar mixture of methyl abietate and abietic acid was heated at 200° C. The isomerization and disproportionation proceeded at the same rate and to the same extent as that of methyl abietate alone.

Isomerization of Methyl Abietate in the Presence of *p*-Toluenesulfonic Acid. Methyl abietate and 5 mole % of *p*-toluenesulfonic acid were mixed thoroughly in a methanol-ether solution and the solvent removed under reduced pressure. The next morning, the system had reached an equilibrium mixture (at room temperature) of 94.5% abietate, 3.5% palustrate, and 1.9% neoabietate. Heating the mixture in sealed tubes at 180° C. for two hours and opening tubes at intervals showed no change in the equilibrium ratios.

Isomerization of Methyl Abietate in Ethanolic Hydrochloric Acid. The isomerization of a 1% solution of methyl abietate in 0.5*N* ethanolic hydrochloric acid was carried out as described previously (*7*). The isomerization reached equilibrium in about seven days (93.0% methyl abietate, 4.2% methyl palustrate, and 2.8% methyl neoabietate). At the end of 24 days, 5.8% of methyl dehydroabietate was observed to be present.

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Convenient O-Alkylation of Phenols

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The preparation of several aryl-methyl ethers by refluxing excess methyl iodide with the corresponding phenols is described. Dimethylformamide was the solvent used, and anhydrous potassium carbonate was the base. Yields for several phenols are given.

THE PREPARATION of aryl-alkyl ethers from phenols is frequently carried out by reaction of an alkali metal phenolate with alkyl halides or sulfates (*5*). In the presence of strong bases, oxidation of the phenol is often a complication. In a search for preparatively useful methods utilizing dipolar aprotic solvents (*1, 4*), the authors have found a particularly convenient system for the synthesis of aryl-methyl ethers.

Simple refluxing of phenols with excess methyl iodide, using anhydrous potassium carbonate as base (*2*) and dimethylformamide as solvent, gives good to excellent results with a variety of phenols as indicated in Table I. Preliminary rate studies indicate that most of the reactions are complete in less than six hours. The purity of the products was determined by gas chromatography and infrared spectroscopy.

Table I

Phenol	Halide	Products	Yield[a] %
Phenol	Methyl iodide	Anisole	80.0
Phenol	Ethyl bromide	Phenetole	77.0
Thymol	Methyl iodide	Thymol methyl ether	74.0
2-Isopropylphenol	Methyl iodide	2-Isopropylanisole	69.5
2,6-Dimethylphenol	Methyl iodide	2,6-Dimethylanisole	76.5
5-Indanol	Methyl iodide	5-Methoxyindane	84.5
1-Naphthol	Methyl iodide	1-Methoxynaphthalene	96.0
2-Naphthol	Methyl iodide	2-Methoxynaphthalene	94.5
p,p'-Biphenol	Methyl iodide	4,4'-Dimethoxybiphenyl	95.5
Catechol	Methyl iodide	Veratrole	91.5
Resorcinol	Methyl iodide	1,3-Dimethoxybenzene	69.5
Hydroquinone	Methyl iodide	1,4-Dimethoxybenzene	85.5
Pyrogallol	Methyl iodide	1,2,3-Trimethoxybenzene	55.0

[a] Based on gas chromatography.

EXPERIMENTAL

General Procedure. In a typical experiment 2.0 grams of the phenol was dissolved in 10.0 ml. of dimethylformamide (reagent grade), 2.0 grams of anhydrous potassium carbonate was added, in addition to 5.0 ml. of reagent grade methyl iodide. The solution was refluxed for 20 hours. The reaction mixture was then poured into 150 ml. of cold water, and extracted twice with 100-ml. portions of ether. The combined ether extracts were washed twice with 10% NaOH solution and twice with distilled water. The ether extract was then dried over anhydrous potassium carbonate, filtered, and concentrated. The crude product was analyzed by gas chromatography using either a 10-foot × ¼-inch column packed with 20% DEGS/60- to 80-mesh Chrom W or a 5-foot × ¼-inch column, containing 20% Apiezon L/60- to 80-mesh Chrom W. The products were also analyzed by infrared spectroscopy.

Preparative Procedure. *p,p′*-Biphenol (62.0 grams, 0.33 mole) was dissolved in 500 ml. of reagent grade dimethylformamide. Anhydrous potassium carbonate, 125.0 grams, and 150.0 grams (1.06 moles) of methyl iodide were added. The mixture was refluxed for 26 hours. The hot solution was then poured into 2 liters of cold water and the product collected by filtration. After washing with water, the product was partially air-dried, then recrystallized once from DMF-methanol to give 48.0 grams (75% yield) of 4,4′-dimethoxybiphenyl, m.p. 177–78° C. [reported 173° C. (*3*)].

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Reaction of *N*-Pentachlorophenyl Ethylenediamine with Phosgene

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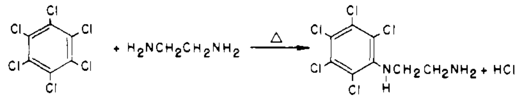
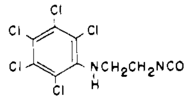
N-Pentachlorophenyl ethylenediamine was converted by treatment with phosgene to the novel cyclic allophanoyl chloride, 1-pentachlorophenyl-3-chlorocarbonyl-2-imidazolidinone. The desired acyclic product, 2-(pentachlorophenylanilino)-ethyl isocyanate, apparently formed as a reaction intermediate, but was not isolable. The fact that this phosgenation proceeded with ring closure despite the feeble basicity of the amino group attached to the polychlorinated aromatic ring attests to the importance of intramolecular proximity effects in governing the course of reactions wherein 5-membered ring formation is possible.

N-Pentachlorophenyl ethylenediamine, I, is available in a virtually quantitative yield from the condensation of hexachlorobenzene with ethylenediamine (*2*). The powerful electron withdrawing character of the pentachlorophenyl group, in combination possibly with a steric hindrance effect, so drastically reduces the basicity of the secondary amino group in I that the compound behaves in many respects as though it were a monoamine. Thus, although three amine hydrogens are present in I, only the two attached to the primary amine function will react with 1) 1,2-alkylene oxides at temperatures as high as 175° C.; 2) acetic anhydride in refluxing pyridine; and 3) epichlorohydrin in the presence of caustic soda (*1*). Furthermore, I analyzes as a monoamine when titrated with either sulfuric acid in aqueous methanol or with perchloric acid in glacial acetic acid. Finally, treatment of I with an excess of the highly reactive phenyl isocyanate in toluene solution for 30 minutes followed by quenching with an excess of di-*n*-butylamine and back-titration with standard hydrochloric acid solution yields an equivalent weight for I closely approximating its molecular weight, indicating again that reaction occurs with one amino group only.



I

The marked tendency for I to behave as a monoamine suggested the possibility of converting this intermediate via phosgenation into 2-(pentachlorophenylanilino)-ethyl isocyanate, II, a molecule which would be unique from the standpoint of containing an isocyanate function and a secondary amine function in a state of stable coexistence. Our interests in II were both academic and commercial in nature, since in addition to possessing sheer novelty value, II represented a potentially interesting biological intermediate and special-purpose component for certain flame-proof polymer systems.



II

Phosgenation of I in *o*-dichlorobenzene solution using the conventional cold-hot, two-stage technique (*4*) proceeded smoothly, hydrogen chloride being evolved vigorously at 130° C. Monitoring of the progress of the phosgena-