The crude carbodiimide obtained from the ether solution could be used without distillation for preparation of quaternized derivatives.

1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride. A mixture of 1.71 g. (0.011 mole) of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide and 1.07 g. (0.0092 mole) of pyridine hydrochloride in 10 ml. of methylene chloride was stirred at room temperature for 3 min. Anhydrous ether (100 ml.) was added dropwise and the crystalline product was collected by filtration. Recrystallization from methylene chloride-ether afford 1.76 g. (99.5%), m.p. 113.5–114.5°.

Anal. Calcd. for $C_8H_{18}N_3Cl$: C, 50.11; H, 9.47; N, 21.92. Found C, 49.76; H, 9.61; N, 22.07.

When scaled up 10–20 fold the yield of carbodiimide hydrochloride was 85–90%, m.p. 108–112.5°.

1-Cyclohexyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride. To a solution of 4.20 g. (0.02 mole) of 1-cyclohexyl-3-(3-dimethylaminopropyl)carbodiimide in 30 ml. of methylene chloride was added 2.14 g. (0.019 mole) of recrystallized pyridine hydrochloride. After 5 min. the mixture was homogenous; 300 ml. of ether was added to precipitate 4.29 g. (94%) of product, m.p. 99–104°.

Anal. Calcd. for $C_{12}H_{24}N_3Cl$: C, 58.64; H, 9.84; N, 7.10; Cl, 14.43. Found: C, 59.14; N, 10.01; N, 16.95; Cl, 14.57.

1-Cyclohexyl-3-(3-dimethylaminopropyl)carbodiimide methiodide (VIa). The crude 1-cyclohexyl-3-(3-dimethylaminopropyl)carbodiimide (IIIC) obtained by dehydration of 22.7 g. (0.10 mole) of the corresponding urea IC was treated with 28.4 g. (0.20 mole) of methyl iodide in 500 ml. of anhydrous ether. After stirring at room temperature for 18 hr. 27 g. (77%) of crystalline product was obtained, m.p. 158–159°. Recrystallization from acetone-ether afforded an analytical sample, m.p. 161.5–163°.

Anal. Calcd. for $C_{13}H_{26}N_3I$: C, 44.45; H, 7.46; N, 11.97. Found: C, 44.46; H, 7.38; N, 11.84.

A portion of VIa was converted to the urea by action of acetic acid in methylene chloride; m.p. 194–195.5° after recrystallization from ethanol-ether.

Anal. Calcd. for $C_{13}H_{28}N_3OI$: C, 42.28; H, 7.64; N, 11.38. Found: C, 42.23; N, 7.75; N, 11.09.

1-Cyclohexyl-3-(3-dimethylaminopropyl)carbodiimide metho-p-toluenesulfonate. Methyl *p*-toluenesulfonate (3.9 g., 0.021 mole) and 1-cyclohexyl-3-(3-dimethylaminopropyl)carbodiimide (3.94 g., 0.019 mole) in 40 ml. of ether were allowed to react at room temperature for 20 hr. The yield of quaternary salt was 6.09 g. (82%), m.p. 164.4–165.4°.

Anal. Calcd. for $C_{20}H_{33}N_3O_3S$: C, 60.72; H, 8.41; N, 10.62. Found: C, 60.80; H, 8.40; N, 10.68.

1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide methiodide. Quaternization of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (IIIA) was carried out in the manner described above for the preparation of VIA. The solid product was recrystallized from chloroform-ethyl acetate; m.p. 106.5–107.5.°

Anal. Calcd. for $C_9H_{20}N_3I$: C, 36.37; H, 6.78; N, 14.14. Found: C, 36.17; H, 6.88; N, 14.17.

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DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE 39, MASS.

RESEARCH INSTITUTE FOR MEDICINE AND CHEMISTRY
CAMBRIDGE 42, MASS.

Reduction of Phenols to Aromatic Hydrocarbons

W. N. MOULTON AND C. G. WADE

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The reduction of phenols to aromatic hydrocarbons is one of the most difficult of organic reactions. Zinc dust distillation, treatment with hydrogen iodide and red phosphorus, and various catalytic hydrogenations have been used with limited success. The two best procedures available appear to be the reduction of aryl diethyl phosphates with sodium or lithium in liquid ammonia[1], and the catalytic hydrogenation of aryl *p*-toluenesulfonates over Raney nickel.[2]

In 1883 Guether[3] reported that phenol could be reduced to benzene and cresol (isomer unspecified) to toluene in low yield by heating with phosphorus trisulfide. The reaction equation given was:

$$8C_6H_4OH + P_2S_3 \longrightarrow 2C_6H_6 + 2(C_6H_5O)_3PO + 3H_2S$$

We have reinvestigated the reaction and studied some modifications which make the reaction more useful.

Our preliminary experiments confirmed Guether's report. For example phenol and phosphorus trisulfide were heated together, the temperature being slowly raised. Between 50 and 100° a large amount of hydrogen sulfide was evolved. No other product was obtained until the temperature reached 300°. Between 300 and 400° a liquid distilled from which benzene was isolated in 18% yield. The results of several similar experiments are recorded in Table I. The temperatures at which the products were obtained varied from 250 to 400°. In each case a black intractable residue remained in the flask. None of the desired reduction product was obtained from *p*-chlorophenol, *p*-aminophenol, resorcinol,

TABLE I

REDUCTION OF INDIVIDUAL COMPOUNDS

Reactants	Products	% Conversion
Phenol	Benzene	18
2-Naphthol	Naphthalene	20
1-Naphthol	Naphthalene	11
2-Hydroxybiphenyl	Biphenyl	18
1-Octanol	Octane and	10
	octene	26
Cyclohexanol	Cyclohexene	65

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(2) G. W. Kenner and M. A. Murray, *J. Chem. Soc.*, S178 (1949).

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or guaiacol. These compounds apparently decomposed as none of the starting materials were recoverable. As shown in Table I aliphatic alcohols largely underwent dehydration, but *n*-octyl alcohol was reduced to octane in 10% yield.

On the basis of the Guether equation only one fourth of phenol would be expected to be reduced, and the yields obtained bore this out. This suggested that if the reaction was carried out on a mixture, one phenol might be selectively reduced. The results of several experiments using mixtures of phenol and a second phenolic compound are given in Table II. The results suggest that the reaction might be useful in the synthesis of polycyclic hydrocarbons using phenol as a coreactant. In the cases shown the product was distilled from the flask as the reaction proceeded. It may be possible to carry out the reaction in a sealed tube and isolate the hydrocarbon by extraction or chromatography. However, we have used only the distillation technique.

TABLE II

REDUCTION OF MIXTURES OF PHENOLS

Reactants (Mole Ratios)	Products	Yield, %
2-Naphthol:Phenol		
1:1	Naphthalene	33
1:3	Naphthalene	67
1:7	Naphthalene	53
	Benzene	14
1-Naphthol:Phenol		
1:1	Naphthalene	18
2-Hydroxybiphenyl:Phenol		
1:3	Benzene	21

The reagent was originally designated phosphorus trisulfide, P_2S_3. However, it has been established that this composition is not a pure compound, but rather a mixture of phosphorus sesquisulfide, P_3S_3, and phosphorus heptasulfide, P_4S_7.[4] The reagent used in our experiments was prepared by igniting a mixture of phosphorus and sulfur in a two to three mole ration in a closed crucible. Neither commercial P_4S_3 or P_4S_7, nor a mixture of the two in the same proportions as P_2S_3, gave satisfactory results. Not all batches of the reagent we prepared were effective in the reaction. In some instances we obtained a material that behaved very similarly to the mixture of commercial phosphorus sulfides with the P_2S_3 composition. There was no visual difference between effective and ineffective reagent. A sample of each new batch was checked using the reduction of 2-naphthol as a test. If the reduction was unsatisfactory, the batch was discarded. The reagent did not deteriorate on standing. The addition of small amounts of free phosphorus or sulfur to inactive reagent had no effect.

No serious effort to isolate any product but the desired hydrocarbon has been made. It would be premature to speculate on the mechanism of the reaction until further studies are made. That the reaction involves a phosphate ester is suggested by the observation that at temperatures from 50–100° a reaction occurs in which hydrogen sulfide is evolved and the phenol reacts to form a high boiling intermediate. No phenol is distilled from the reaction even at temperatures more than a hundred degrees above its boiling point. Walling[5] has recently observed that thiophenol and triethyl phosphite react at 145° in presence of a free radical catalyst to give benzene and triethyl phosphorothionate in 10–15% yield.

EXPERIMENTAL

Phosphorus trisulfide. An intimate mixture of 31 g. of phosphorus and 48 g. of sulfur were ignited in an unglazed crucible buried in a pail of sand. When the reaction was complete and the crucible cold the reagent was removed by breaking up the crucible. The reagent was gummy at first, but completely crystallized in 24 hr. Each batch was tested using the procedure which follows.

Reduction procedure. A mixture of 70 g. of phenol and 60 g. of phosphorus sulfide was placed in a 20-ml. Claisen flask, fitted with a thermometer reaching nearly to the bottom of the flask. A second thermometer was placed in the side arm to measure the vapor temperature of the distillate. As the mixture was slowly heated to 150° hydrogen sulfide was evolved. After holding the temperatures at 150° for 30 min. heating was increased. At pot temperatures above 300° benzene distilled. The reaction was discontinued when the temperature reached 400° at which point the black residue foamed up to nearly fill the flask. The distillate (10.5 g.) was redistilled to give 7.3 g. (12.5%) of benzene, b.p. 80–81°, n_D^{25} 1.4976.

All reductions were carried out by essentially the same procedure. Yields reported in tables are for products after one distillation or crystallization, and are based on total phenol used. In mixed reactions the mole ratio of phosphorus trisulfide to combined phenols was the same as described above.

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DEPARTMENT OF CHEMISTRY
SOUTHERN ILLINOIS UNIVERSITY
CARBONDALE, ILL.

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