Notes A department for short papers of immediate interest.

N-Methylpyrrolidone as Solvent for Reaction of Aryl Halides with Cuprous Cyanide[1]

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Received September 28, 1960

The reaction of aryl chlorides and bromides with cuprous cyanide to yield nitriles is a useful reaction which has been carried out in the presence and absence of solvents.[2] The advantage of using *N*-methylpyrrolidine as a reaction medium because of its ability to dissolve cuprous cyanide has been pointed out.[3] Although we have not studied this method in great detail, we report our findings now because of their possible utility.

As can be seen from the results summarized in Table I, the yields are generally near 90%. One advantage in the use of *N*-methylpyrrolidone is the shorter time needed.[4] Most runs were carried out with about 0.1 mole[5] of halide and an 80% excess of cuprous cyanide in 100 ml. of *N*-methylpyrrolidone at reflux (202°). Other studies[5] showed that the amount of *N*-methylpyrrolidone can be decreased markedly. Lower temperatures than that of refluxing solvent (202°) can be used (see Footnotes *f*, *g*, and *h* in Table I) but this variable has not been much studied. 1-Chloronaphthalene afforded a high yield[6] but insufficient work was done with chloro compounds to generalize.

To our knowledge, the synthesis of cinnamononitrile represents the first conversion of a vinylic halide to a nitrile by this method.

We hope to utilize the fact that cuprous cyanide dissolves in *N*-methylpyrrolidone at about 90° to carry out relative rate measurements on a series of aryl halides.

TABLE I

REACTIONS OF ARYL AND HETEROCYCLIC HALIDES WITH CUPROUS CYANIDE IN *N*-METHYLPYRROLIDONE

Halide[a]	Reaction Time (hr.)	Yield,[b] %
1-Bromonaphthalene	3	89
1-Bromonaphthalene	3	60[c]
1-Chloronaphthalene	24	87
2-Bromonaphthalene	3	90[d]
2-Bromonaphthalene	3	88[e]
2-Bromonaphthalene	3	85[f]
2-Bromonaphthalene	11	84[g]
9-Bromophenanthrene	4.5	92
β-Bromostyrene	2	92
2-Bromothiophene	19	67[h]
2-Chloroquinoline	4.5	42
4-Bromoisoquinoline	2.5	90
1-Bromobenzo[c]-phenanthrene	1.5	83
Methyl 2-chloro-3,5,6-trimethylbenzoate	3	82

[a] All experiments in Table I involved 0.1 mole of halide and 0.18 mole of cuprous cyanide in 100 ml. of distilled *N*-methylpyrrolidone[7] at reflux (202°) unless otherwise noted. [b] Yield represents per cent of material, distilled or recrystallized, agreeing well with the properties described in the literature for the pure substances. All products after sodium fusion gave negative tests for halogen. [c] In refluxing (165°) dimethylacetamide.[8] [d] The yield in a 0.5-mole run (4 hr. heating, 100 ml. of *N*-methylpyrrolidone) was 95%. [e] Only 0.15 mole of cuprous cyanide used. [f] Same as *e* except temperature held at 180°. [g] Same as *e* except temperature held at 155 ± 5°. [h] In a similar run at 180–190° for 34 hours the yield was 55%.

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[1] This work was supported by grant G-9482 from the National Science Foundation.

[2] For a review see L. Friedman and H. Shechter, *J. Org. Chem.*, **26**, 2522 (1961). In this paper the advantage of using ferric chloride solution in working up the reaction mixture is pointed out.

[3] M. S. Newman and D. K. Phillips, *J. Am. Chem. Soc.*, **81**, 3667 (1959).

[4] For example, M. Newman, *Org. Syntheses*, Coll. Vol. III, 633 (1955) reports a yield of 82–90% of 1-naphthonitrile from 1-bromonaphthalene after fifteen hours of heating.

[5] In every case in which a run considerably larger than 0.1 mole was made, the yield of purified product was over 90%. For example, Dr. M. V. George prepared pure *p*-tolunitrile in 95% yield from *p*-bromotoluene (85.5 g.) in a *N*-methylpyrrolidone (100 ml.) by heating for two hours at reflux.

[6] Only one experiment with 1-chloronaphthalene was made. The long reaction time (twenty-four hours) might be unnecessary.

[7] We acknowledge with thanks a generous gift of *N*-methylpyrrolidone from the Antara Chemical Co.

[8] We acknowledge with thanks a generous gift of *N*,*N*-dimethylacetamide from the du Pont Company.

A Convenient Synthesis of Water-Soluble Carbodiimides

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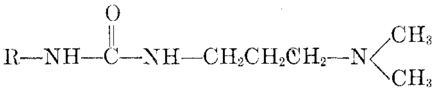
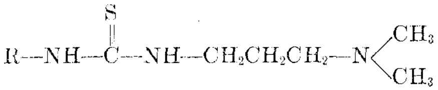
The utility of the carbodiimide procedure for formation of the amide bond has been well established by the synthesis of many complex peptides.[3] Dicyclohexyl- and diisopropylcarbodiimides have been commonly used as the condensing agents; however, the corresponding ureas and acylureas[4] frequently have solubility properties similar to the peptides, rendering separation of the products difficult. An earlier publication from one of these laboratories described the preparation of some acid-soluble and water-soluble carbodiimides.[5] With these reagents the by-product ureas and acylureas were easily removed by washing with dilute acid or water.

In this note we wish to describe some new acid- and water-soluble carbodiimides prepared from commercially available starting materials. The most generally useful compounds are 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (IIIA) and the corresponding hydrochloride salt. Other compounds prepared and evaluated include 1-cyclohexyl-3-(3-dimethylaminopropyl)carbodiimide (IIIC), the hydrochloride salt, and several quaternized derivatives (VI). Derivatives of 1-isopropyl-3-(3-dimethylaminopropyl)carbodiimide (IIIB) are too hygroscopic to be of practical value.



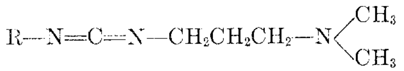
$$R-NH-\overset{\displaystyle O}{\overset{\|}{C}}-NH-CH_2CH_2CH_2-N\left<\begin{matrix}CH_3\\CH_3\end{matrix}\right.$$

I



$$R-NH-\overset{\displaystyle S}{\overset{\|}{C}}-NH-CH_2CH_2CH_2-N\left<\begin{matrix}CH_3\\CH_3\end{matrix}\right.$$

II



$$R-N=C=N-CH_2CH_2CH_2-N\left<\begin{matrix}CH_3\\CH_3\end{matrix}\right.$$

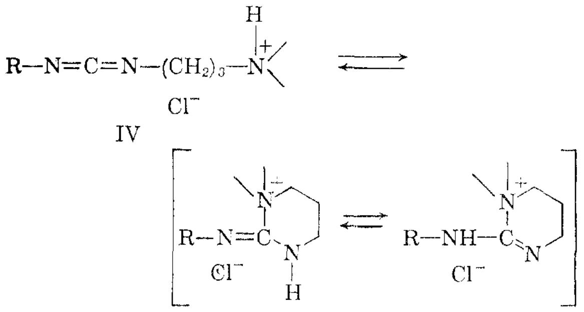
III

A. R = C_2H_5-
B. R = $(CH_3)_2CH-$
C. R = $C_6H_{11}-$

The basic carbodiimides (III) were prepared either by dehydration of the corresponding urea (I) or by removal of the elements of hydrogen sulfide from the corresponding thiourea (II). The desulfurization procedure[6] is not recommended, however, in that large quantities of mercuric oxide and long reaction times are required, and the product is likely to be contaminated with sulfur-containing impurities.

Dehydration of the basic ureas was effected with *p*-toluenesulfonyl chloride and triethylamine in methylene chloride solution. This is a modification of the procedure of Amiard and Heymes[7] for the dehydration of 1,3-dicyclohexylurea in which a large volume of pyridine was used both as base and as solvent.

Hydrochloride salts of the basic carbodiimides were prepared by metathesis with pyridine hydrochloride in methylene chloride solution; addition of ether precipitated the products. The hydrochlorides of 1-alkyl-3-(3-dimethylaminopropyl)-carbodiimides (III) appear to be capable of existence in two structurally isomeric forms. An infrared absorption spectrum in chloroform solution has the 2130 cm.$^{-1}$ band characteristic of the —N=C=N— chromophore. The infrared absorption of the crystalline solid (Nujol or potassium bromide dispersion), however, has ν_{max} at 3250 cm.$^{-1}$ and at 1700 cm.$^{-1}$, characteristic of —NH— and C=N— respectively. We would therefore like to suggest a ring-chain tautomerism IV ⇄ V for these compounds.

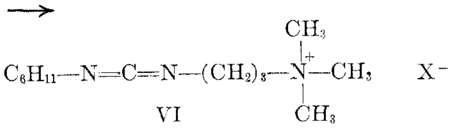


IV

V

Quaternized salts of the basic carbodiimides were prepared in ether solution from which the products (VI) separated spontaneously.

$IIIC + CH_3X \longrightarrow$



$$C_6H_{11}-N=C=N-(CH_2)_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|+}}{N}}-CH_3 \qquad X^-$$

VI

a. X = I
b. X = OTs

The basic ureas (I) and thioureas (II) were prepared by reaction of the appropriate isocyanate or isothiocyanate, respectively, with *N,N*-dimethyl 1,3-propanediamine. An improved procedure for preparation of cyclohexyl isocyanate from cyclohexylamine and phosgene was developed; this isocyanate could be utilized without isolation for the preparation of 1-cyclohexyl-3-(3-dimethylaminopropyl)urea (IC).

Peptides have been synthesized in high yields and in very pure form with the carbodiimides described in this note. The reagents have also been utilized to form amide bonds in proteins.

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(2) Research Institute for Medicine and Chemistry, Cambridge 42, Mass.

(3) For a recent review see M. Goodman and G. W. Kenner, *Advances in Protein Chemistry,* **12,** 488 (1957).

(4) H. G. Khorana, *Chem. and Ind.,* 1087 (1955); J. C. Sheehan, M. Goodman, and G. P. Hess, *J. Am. Chem. Soc.,* **78,** 1367 (1956).

(5) J. C. Sheehan and J. J. Hlavka, *J. Org. Chem.,* **21,** 439 (1956).

(6) H. G. Khorana, *Chem. Revs.,* **53,** 145 (1953).

(7) G. Amiard and R. Heymes, *Bull. Soc. Chim. France,* 1360 (1956).

EXPERIMENTAL[8]

1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (IIIA). *Desulfurization of thiourea* IIA. To a cooled solution of 17.43 g. (0.2 mole) of ethyl isothiocyanate in 50 ml. of ether was added dropwise a solution of 20.44 g. (0.2 mole) of *N,N*-dimethyl-1,3-propanediamine in 50 ml. of ether. After 5 hr. at room temperature the ether was evaporated under reduced pressure; the residual oil was used without purification for subsequent experiments.

The crude thiourea IIA derived from 0.2 mole of ethyl isothiocyanate was dissolved in 150 ml. of dry methylene chloride. To this solution was added 108.5 g. (0.5 mole) of yellow mercuric oxide and the mixture was shaken mechanically for 20 hr. Another 21.2 g. (0.1 mole) portion of the mercuric oxide was then added and the shaking was continued for an additional 5 hr. At this time a probe test[9] for unchanged thiourea was negative. The mixture was filtred under dry nitrogen pressure, and the methylene chloride removed from the filtrate by evaporation under reduced pressure. Distillation of the residue under reduced pressure afforded 22.9 g. (74%) of carbodiimide IIIA, b.p. 47–48° (0.27 mm.), n_D^{25} 1.4582.

Anal. Calcd. for $C_8H_{17}N_3$: C, 61.89; H, 11.04; N, 27.07. Found: C, 61.53; H, 11.11; N, 27.81.

1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (IIIA). *Dehydration of urea* IA. To a solution of 20.5 g. (0.288 mole) of "practical" ethyl isocyanate in 200 ml. of anhydrous ether was added slowly 28.9 g. (0.280 mole) of *N,N*-dimethyl-1,3-propanediamine in 100 ml. of ether; the reaction temperature was moderated by means of external cooling. After stirring at room temperature for 2 hr. the ether was removed under reduced pressure leaving a quantitative yield of crude 1-ethyl-3-(3-dimethylaminopropyl)urea as a pale yellow oil. This crude material was used directly for preparation of the carbodiimide (IIIA).

To a solution of 42 g. (0.24 mole) of crude 1-ethyl-3-(3-dimethylaminopropyl)urea (IA) in 750 ml. of methylene chloride and 130 ml. of triethylamine was added a solution of 91.3 g. (0.48 mole) of recrystallized *p*-toluenesulfonyl chloride in 500 ml. of methylene chloride. The temperature of the reaction mixture was maintained at 5° or less during the addition by means of external cooling. After the addition of the *p*-toluenesulfonyl chloride the reaction was allowed to warm to room temperature, and then was heated under reflux for 3 to 4 hr. The reaction mixture was stirred with three 200-ml. portions of 40% aqueous potassium carbonate; the solids and aqueous phase were removed after each treatment and were washed thoroughly with methylene chloride. The combined methylene chloride phases were concentrated and the residual oil extracted with several portions of ether. After evaporating the ether the residue was distilled to give 19.3 g. (51%) of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide, b.p. 53–54° (0.60 mm.), n_D^{22} 1.4594.

1-Isopropyl-3-(3-dimethylaminopropyl)carbodiimide (IIIB) via 1-isopropyl-3-(3-dimethylaminopropyl)urea (IB). The urea IB was prepared in the same manner as the ethyl analog IA. An extremely hygroscopic solid, m.p. 62–69°, was obtained upon removal of solvent. A small sample was purified by sublimation, m.p. 66–71°.

Anal. Calcd. for $C_9H_{21}N_3O$: N, 22.44. Found: N, 22.61.

Dehydration of the urea IB by the *p*-toluenesulfonyl chloride-triethylamine procedure as described above for the 1-ethyl homolog afforded 1-isopropyl-3-(3-dimethylaminopropyl)carbodiimide (IIIB), b.p. 57–59° (0.7 mm.), n_D^{25} 1.4545.

Anal. Calcd. for $C_9H_{19}N_3$: C, 63.86; H, 11.31; N, 24.83. Found: C, 64.21; H, 11.39; N, 24.69.

1-Cyclohexyl-3-(3-dimethylaminopropyl)carbodiimide (IIIC). *Desulfurization of thiourea* IIA. Carbon disulfide (20.14 g., 0.26 mole) was added slowly to a stirred solution of 57.47 g. (0.53 mole) of cyclohexylamine in 400 ml. of dry ether at 0°. The colorless solid was collected by filtration, dissolved in 750 ml. of water, and treated with 70 g. (0.26 mole) of mercuric chloride at 90° for a few minutes. Steam distillation removed the cyclohexyl isothiocyanate[10] from the reaction mixture; the crude product, recovered from the distillate by extraction with ether, amounted to 28.0 g. (76%). To a cooled solution of this isothiocyanate in 100 ml. of ether was added 20.2 g. (0.20 mole) of *N,N*-dimethyl-1,3-propanediamine in 100 ml. of ether. The thiourea separated during the reaction; 32 g. (66% based on the crude cyclohexyl isothiocyanate), m.p. 70.4–71.0°.

Anal. Calcd. for $C_{12}H_{25}N_3S$: C, 59.20; H, 10.35; N, 17.26. Found: C, 59.18; H, 10.37; N, 17.52.

A solution of 15 g. (0.062 mole) of 1-cyclohexyl-3-(3-dimethylaminopropyl)thiourea in 90 ml. of methylene chloride was shaken for 20 hr. with 53.55 g. (0.25 mole) of yellow mercuric oxide. Since some thiourea still was present in the reaction mixture[11] an additional 13.4 g. (0.062 mole) of mercuric oxide was added and the shaking continued for 12 hr. The solution was filtered under nitrogen, the solvent removed, and the residue distilled. The yield of carbodiimide was 9.15 g. (71%) b.p. 89.5–91.5 (0.40 mm.), n_D^{25} 1.4844.

Anal. Calcd. for $C_{12}H_{23}N_3$: C, 68.84; H, 11.07; N, 20.07. Found: C, 68.72; H, 10.94 N, 19.98.

1-Cyclohexyl-3-(3-dimethylaminopropyl)carbodiimide (IIIC). *Dehydration of urea* IC. To a solution of 54. 5 g. (0.551 mole) of phosgene in 350 ml. of benzene was added slowly a solution of 13.6 g. (0.137 mole) of cyclohexylamine in 100 ml. of benzene. This slurry was stirred for 16 hr. at 60–75° during which the solids dissolved. The resulting pale yellow solution was refluxed vigorously for 2 hr., after which approximately half the benzene was distilled. The solution of cyclohexyl isocyanate[11] remaining in the flask was cooled with an ice bath, and a solution of 14.0 g. (0.137 mole) of *N,N*-dimethyl-1,3-propanediamine in 200 ml. of ether was added. After stirring at room temperature for 3 hr. the solvents were removed under reduced pressure. Trituration of the residue with ether afforded 28.6 g. (92%) of crude urea, m.p. 79.5–84°. Recrystallization from ether raised the m.p. to 90.4–91.0°.

Anal. Calcd. for $C_{12}H_{25}N_3O$: C, 63.39; H, 11.08; N, 18.49. Found: C, 63.40; H, 11.08; N, 18.35.

To a solution of 1-cyclohexyl-3-(3-dimethylaminopropyl)-urea (46.32 g., 0.204 mole) in 600 ml. of methylene chloride and 100 ml. of triethylamine was added a solution of 58.0 g. (0.306 mole) of *p*-toluenesulfonyl chloride in 400 ml. of methylene chloride; the temperature was kept below 5° by external cooling. After completing the addition the mixture was stirred for 30 min. at room temperature and finally for 2 hr. under gentle reflux. The cooled mixture was extracted with 1.0 l. of 10% aqueous potassium carbonate; the organic phase was dried over magnesium sulfate and the solvents removed under reduced pressure. The residue was freed of triethylamine by dissolving in toluene and again evaporating under reduced pressure. The residue was triturated with several portions of ether to remove the carbodiimide from a resinous byproduct. After evaporating the ether distillation afforded 28.46 g. (67%) of product, b.p. 104° (0.8 mm.).

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[8] All melting points are corrected. Analyses were by S. M. Nagy, Massachusetts Institute of Technology, Cambridge, Mass., or by A. Bernhardt, Max Planck Institute, Mulheim, Germany.

[9] This test constitutes addition of 2 drops of 0.25*M* silver nitrate solution and 4 drops of ammonium hydroxide to a small aliquot of the reaction mixture. Appearance of a brown precipitate indicates the presence of thiourea.

[10] A. Skita and H. Rolfer, *Ber.*, **53**, 1242 (1920).

[11] Pure cyclohexyl isocyanate may be obtained by fractional distillation, b.p. 53°/11 mm.; W. Siefken, *Ann.*, **562**, 75 (1949) reports b.p. 54°/11 mm.

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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Reduction of Phenols to Aromatic Hydrocarbons

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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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(1) G. W. Kenner and N. R. Williams, *J. Chem. Soc.*, 552 (1955).

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

(3) A. Geuther, *Ann.*, **221**, 55 (1883).