mixed melting point of the picrate with the one from the product obtained by dehydration of the carbinol was not depressed.

Anal. Calcd. for $C_{15}H_{16}N_4O_7$: N, 15.38. Found: N, 15.19.

m-N-Ethylaminophenylmethylcarbinol (V).—The general procedure of Emerson and Mohrman[5] was employed. In a 300-cc. magnesium citrate bottle were placed 16.7 g. of *m*-nitrophenylmethylcarbinol, 2 g. of sodium acetate, 13.2 g. of acetaldehyde and 3–5 g. of Raney nickel. After complete reduction the Raney nickel was removed by filtration, and the alcohol was removed by evaporation. About 80 cc. of ether was added to the resulting slush, and any solid material was filtered. The resulting ether solution was dried over sodium sulfate, the solvent removed, and the residue distilled in a 25-cc., modified Claisen flask. The slightly yellow product boiled at 135–138° (2 mm.), $n^{20}D$ 1.5620. The yield was 12 g. or 73% of the theoretical amount.

Anal. Calcd. for $C_{10}H_{15}ON$: C, 72.68: H, 9.15. Found: C, 72.82; H, 9.01.

m-N-Ethyl-N-acetylaminophenylmethylcarbinol (VI).—In a 300-cc. Erlenmeyer flask was placed 6 g. of *m*-N-ethylaminophenylmethylcarbinol suspended in 60 cc. of water. To this was added 5 g. of concentrated hydrochloric acid and the suspension shaken well until the *m*-N-ethylaminophenylmethylcarbinol dissolved. This solution was then heated to 50° and 6 g. of acetic anhydride was added, immediately followed by 6 g. of sodium acetate. The resulting solution was well mixed and allowed to stand at 50°, for one to two hours. The solution was cooled, extracted with 400 cc. of ether and dried over sodium sulfate. The ether was removed and the residue distilled in a 10-cc. modified Claisen flask. The slightly yellow, viscous oil boiled at 160–162° (0.5 mm.), $n^{20}D$ 1.5390. The yield was 3 g. or 40% of the theoretical. Considerable resinification occurred at the high temperature necessary for distillation. Usually the excess acetic acid and starting material, *m*-N-ethylaminophenylmethylcarbinol, were removed by distillation and the crude residue used in the subsequent attempted dehydration.

Anal. Calcd. for $C_{12}H_{17}O_2N$: C, 69.53; H, 8.26. Found: C, 69.56; H, 8.35.

Summary

Attempted dehydration of *m*-N-methylaminophenylmethylcarbinol over activated alumina led to a disproportionation product, *m*-N-methylaminoethylbenzene. Attempts to dehydrate two related carbinols gave no identifiable products.

URBANA, ILLINOIS RECEIVED NOVEMBER 16, 1945

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF WINTHROP CHEMICAL COMPANY, INC.]

Water-Insoluble Forms of Thiamine and Niacin

BY WOLFGANG HUBER, WERNER BOEHME AND S. C. LASKOWSKI

The need for water-insoluble forms of thiamin, niacin and riboflavin for the enrichment of corn grits and white rice has been pointed out by the Food and Nutrition Board of the National Research Council.[1] Since these cereals are customarily rinsed before cooking, the water-soluble vitamins previously sprayed on the exterior surfaces of the particles are removed, thus obviating this standard method of enrichment.

The present report describes several avenues of approach which have been pursued in these laboratories in order to obtain water-insoluble forms of thiamine and niacin without losing the biological activity. In the case of thiamine, salts were prepared with various derivatives of high-molecular carboxylic and sulfonic acids, including a number of anionic wetting agents. Thus, salts were prepared with several alkylsulfuric acids,[2] with cholestenone-6-sulfonic acid and with methane-1,1-bis-(2-hydroxy-3-naphthoic acid). With the wetting agents only thiamine 2-ethylhexylsulfate was isolated in crystalline form, while all alkyl sulfates of higher molecular weight separated as oils. The thiamine salts of isopropylnaphthalenesulfonic acid and di-octylsulfosuccinic acid also separated in non-crystalline form while the thiamine salt of dibutylsulfosuccinic acid was found to be water-soluble. With cholestenone-6-sulfonic acid as well as with methane-1,1-bis-(2-hydroxy-3-naphthoic acid), thiamine formed water-insoluble solids which could be purified from organic solvents to give well defined crystalline compounds.

In the niacin series neither the acid nor the amide formed satisfactory salts with methane-1,1-bis-(2-hydroxy-3-naphthoic acid) or 2-ethylhexylsulfuric acid. Apparently, the basicity of the ring nitrogen is so far reduced by the presence of a carboxyl in the β-position that a salt will not form.

The preparation and the water solubilities of a series of *n*-alkyl esters of nicotinic acid have recently been reported.[3] Prior to this publication a series of alkyl nicotinates had been prepared in these laboratories and the compounds investigated for their possible value as water-insoluble derivatives. We find that our data are in good agreement with those of Badgett, *et al.*, except for some preparatory details which will be reported in the experimental part. From a practical point of view the enrichment of cereals with alkyl nicotinates has some objections, since these compounds are odoriferous, somewhat unstable oils. However, esterification increased the basicity of the ring nitrogen sufficiently to allow the formation of salts with methane-1,1-bis-(2-hydroxy-3-naphthoic acid). These are odorless, pale yellow solids of very low water solubility, which can be purified by recrystallization from organic solvents.

(1) Gunderson, *Science*, **98**, 277 (1943).

(2) Tergitol series of wetting agents, Carbide & Carbon Chemicals Corp., New York, N. Y.

(3) Badgett, Provost, Ogg and Woodward, THIS JOURNAL, **67**, 1135 (1945).

Various derivatives of nicotinamide also have been prepared. Thus the reaction between *p*-aminobenzoic acid and nicotinyl chloride hydrochloride gave N-(*p*-carboxyphenyl)-nicotinamide as pale cream-colored crystals. Since it appeared that the electronegativity of the ring nitrogen was reduced by the presence of a carboxyamide group in the β-position it seemed reasonable to assume decreased acidity in the carboxyamide radical, perhaps even to the extent of allowing the amide nitrogen to undergo some of the usual amine reactions. This was found to be the case in several instances. Thus, equimolecular parts of nicotinamide and phenyl isocyanate, on being heated in a sealed tube at 150°, gave N-(phenylcarbamyl)-nicotinamide in good yield. The reaction between 6-methoxy-8-aminoquinoline and nicotinyl chloride hydrochloride gave N-(6-methoxy-8-quinolyl)-nicotinamide as pale yellow, water-insoluble needles.

The water solubilities of most of the compounds studied in this investigation are given in Table I. Since the rinsing of enriched cereals would hardly result in saturation, the solubility data represent the maximum possible vitamin loss.

TABLE I

SOLUBILITY OF THIAMINE AND NIACIN DERIVATIVES IN WATER

Compound	Solubility in 100 ml. of water at 25°, g.
Thiamine derivatives	
Chloride hydrochloride	>92
2-Ethylhexylsulfate	2.46
Methane-1,1-bis-(2-hydroxy-3-naphthoate)	0.003
Cholestenone-6-sulfonate	0.004
Niacin derivatives	
Nicotinic acid	1.73
N-(*p*-Carboxyphenyl)-nicotinamide	0.020
N-(Phenylcarbamyl)-nicotinamide	0.010
N-(6-Methoxy-8-quinolyl)-nicotinamide	0.001
Ethyl nicotinate	5.0
Ethyl nicotinate methane-1,1-bis-(2-hydroxy-3-naphthoate)	0.050
Butyl nicotinate	0.253
Butyl nicotinate methane-1,1-bis-(2-hydroxy-3-naphthoate)	0.004
Calcium nicotinate	2.27

Biological Activity

Some of the thiamine salts were assayed biologically in accordance with the method described in the U. S. Pharmacopoeia XII at a dosage equivalent to thiamine on a molecular basis.[4] In the case of thiamine methane-1,1-bis-(2-hydroxy-3-naphthoate) the activity was determined with two assay and two reference levels, thus allowing the calculation of the standard error.[5] The results as summarized in Table II show that in all the tested salts the full biological activity of thiamine is retained. An acid or alkaline solution of some of the water-insoluble niacin derivatives was tested by Dr. A. Arnold of these laboratories for niacin activity by the microbiological procedure as described in the U. S. Pharmacopoeia XII with *L. arabinosus* as the test organism. The results of these tests are shown in Table III. It will be seen that solution in dilute sodium hydroxide immediately before placing the test substances into the medium usually did not yield as much activity as when the test substances were allowed to remain in dilute sodium hydroxide at room temperature overnight. Some of the niacin derivatives, being insoluble in dilute alkali, were added to the medium in dilute sulfuric acid solution. The test results are taken to indicate that the organism can only utilize the hydrolyzed derivative. In the investigated cases such hydrolysis is achieved to a varying degree by treatment with dilute sodium hydroxide, whereas treatment with dilute sulfuric acid did not hydrolyze these compounds to an extent discernible by microbiological assay. This, however, is not necessarily a contraindication for the use of these compounds in the enrichment of cereals since it has been shown that animals are able to break up and utilize niacin combinations toward which bacteria show little activity.[3,6]

TABLE II

BIOLOGICAL ACTIVITY OF THIAMINE SALTS

Compound	U. S. P. units per gram of salt Calcd.	Found
2-Ethylhexylsulfate	172,000	Not less than 172,000
Cholestenone-6-sulfonate	94,300	Not less than 94,300
Methane-1,1-bis-(2-hydroxy-3-naphthoate)	164,000	194,200 ± 15%[a]

[a] See ref. 5.

TABLE III

BIOLOGICAL ACTIVITY OF NIACIN DERIVATIVES

Compound	Treatment	Activity
Butyl nicotinate methane-1,1-bis-(2-hydroxy-3-naphthoate)	0.1 *N* NaOH before use	Full
Ethyl nicotinate methane-1,1-bis-(2-hydroxy-3-naphthoate)	0.1 *N* NaOH before use	65%
	1 *N* NaOH overnight	Full
N-(Phenylcarbamyl)-nicotinamide	0.1 *N* NaOH before use	62%
	1 *N* NaOH overnight	Full
N-(*p*-Carboxyphenyl)-nicotinamide	0.1 *N* NaOH before use	No
	1 *N* NaOH overnight	73%
Butyl nicotinate	0.1 *N* H_2SO_4 before use	No
Ethyl nicotinate	1 *N* H_2SO_4 overnight	No
N-(6-Methoxy-8-quinolyl)-nicotinamide	1 *N* H_2SO_4 overnight	No

(4) The assays were carried out by the Food Research Laboratories Inc., Long Island City, N. Y.

(5) Calculated according to the procedure of Bliss and Marks. *Quart. J. Pharm. Pharmacol.*, **12**, 182 (1939).

(6) For details see the excellent review of Elvehjem and Teply. *Chem. Rev.*, **33**, 185 (1943).

Experimental[7]

4-Methyl-5-β-hydroxyethyl-N-{[2-methyl-4-aminopyrimidyl-(5)]-methyl}-thiazolium 2-Ethylhexylsulfate.—A solution of 6.74 g. (0.02 mole) of thiamine chloride hydrochloride in 25 ml. of cold water was mixed with 18.6 g. (0.02 mole) of a 25% aqueous solution of sodium 2-ethylhexylsulfate.[8] Crystallization began after fifteen minutes and was completed by cooling in an ice-bath for several hours. The colorless crystals were filtered off and washed with cold water. After one recrystallization from a large excess of hot water, 5.2 g. (38%) of glistening rectangular plates were obtained; m. p. 148–149°.

Anal. Calcd. for $C_{28}H_{52}N_4O_9S_3$: C, 49.15; H, 7.61; N, 8.18. Found: C, 49.31; H, 7.33; N, 7.86.

When the ratio of sodium 2-ethylhexylsulfate was increased to 2:1, which is the combining ratio of the salt, the solution remained clear and no precipitation took place after cooling for three days.

4-Methyl-5-β-hydroxyethyl-N-{[2-methyl-4-aminopyrimidyl-(5)]-methyl}-thiazolium Methane-1,1-bis-(2-hydroxy-3-naphthoate).—Six and seven-tenths grams (0.02 mole) of thiamine chloride hydrochloride and 4.5 g. (96% assay, 0.02 mole) of sodium methane-1,1-bis-(2-hydroxy-3-naphthoate)[9] were each dissolved in 100-ml. portions of water. The two solutions were then simultaneously run into 200 ml. of water during thirty minutes with vigorous stirring. Precipitation began immediately and stirring was continued for another hour in order to ensure homogeneity. The precipitate was filtered off, washed with water until free of chloride ion and dried at 60°, *in vacuo*. The pale yellow solid (12.6 g. = 97.5%) was recrystallized twice from 80% aqueous, peroxide-free dioxane to give pale yellow, fine needles, m. p. 202–205° (dec.).

Anal. Calcd. for $C_{35}H_{32}N_4O_7S$: C, 61.03; H, 5.27; N, 8.14. Found: C, 61.22; H, 5.15; N, 8.09.

4-Methyl-5-β-hydroxyethyl-N-{[2-methyl-4-aminopyrimidyl-(5)]-methyl}thiazolium Cholestenone-6-sulfonate.—Using the same procedure as for the "methane" salt, 0.85 g. (0.0025 mole) of thiamine chloride hydrochloride and 2.17 g. (0.005 mole) of cholestenone-6-sulfonic acid[10] gave 2.3 g. (79%) of a white solid which, after two recrystallizations from 95% ethanol, crystallized in small, white needles, m. p. 209–212° (dec.).

Anal. Calcd. for $C_{66}H_{102}N_4O_9S_3$: C, 66.52; H. 8.63; N, 4.70. Found: C, 66.68; H. 8.90; N, 4.78.

N-(p-Carboxyphenyl)-nicotinamide.—Twenty grams (0.154 mole) of nicotinic acid was refluxed with 100 ml. of thionyl chloride for one-half hour and the excess thionyl chloride removed *in vacuo*. Four hundred milliliters of dry pyridine and 22.3 g. (0.163 mole) of *p*-aminobenzoic acid was added to the residual nicotinyl chloride hydrochloride. The mixture was warmed on the steam-bath for three hours and then allowed to cool overnight. The excess pyridine was removed *in vacuo* and the residue was taken up in dilute aqueous sodium carbonate. The alkaline solution was charcoaled, filtered and neutralized with acetic acid. A slightly pink precipitate was obtained (21.0 g. = 53.4%). After two recrystallizations from a large volume of 95% ethanol, pale cream-colored crystals separated, m. p. 303.5–305° (dec.).

Anal. Calcd. for $C_{13}H_{10}N_2O_3$: C, 64.46; H, 4.13; N, 11.65. Found: C, 64.18; H, 4.26; N, 11.33.

N-(Phenylcarbamyl)-nicotinamide.—A mixture of 6.6 g. (0.05 mole) of nicotinamide and 5.9 g. (0.05 mole) of phenyl isocyanate was heated in a sealed tube, first for two hours at 100° and then for two hours at 150°. After cooling, the reaction mixture was taken up with warm dilute ethanol, filtered and cooled overnight in the refrigerator. The precipitate was filtered off and recrystallized from dilute ethanol. Thus, 8 g. (64%) of white, long, rectangular plates was obtained, m. p. 215–216°.

Anal. Calcd. for $C_{13}H_{11}N_3O_2$: C, 64.72; H, 4.60; N, 17.42. Found: C, 64.86; H, 4.37; N, 17.25.

N-(6-Methoxy-8-quinolyl)-nicotinamide.—Forty grams (0.308 mole) of nicotinic acid was heated at 100° for one-half hour with 100 ml. of dry pyridine and 25 ml. of thionyl chloride. Thirty-eight grams (0.23 mole) of 6-methoxy-8-aminoquinoline[11] in 100 ml. of dry pyridine was then added and the mixture heated one-half hour longer on the steam-bath. After cooling, the precipitate was filtered from the greenish-black solution and washed with pyridine. After two recrystallizations from dilute ethanol 30 g. (49%) of finely matted, pale yellow needles was obtained, m. p. 175–177°.

Anal. Calcd. for $C_{16}H_{13}N_3O_2$: C, 68.81; H, 4.66; N, 15.05. Found: C, 68.47; H, 4.72; N, 15.01.

Esters of Nicotinic Acid.—The following method was utilized, which differs somewhat from the one used by Badgett, *et al.*[3] Niacin (0.5 mole) was refluxed with purified thionyl chloride (2.5 mole) for one hour. The excess thionyl chloride was recovered by distillation *in vacuo* and to the residual light cream-colored nicotinyl chloride hydrochloride dry pyridine (1 mole) was added with subsequent heating of the mixture for one-half hour. Then the alcohol (1.3 mole) was added in a very fine stream, while refluxing was continued for one hour. After cooling, the precipitated pyridine hydrochloride was filtered and washed well with ether. The filtrate was diluted with ether to a total volume of 650 ml., chilled and filtered to remove additional pyridine hydrochloride. After removal of ether and excess alcohol, the crude ester was purified by distillation *in vacuo* under nitrogen. This procedure has been applied to the preparation of the following nicotinates[3] with average yields of over 80% of theory: ethyl, propyl, butyl, *n*-amyl, isoamyl,[12] hexyl ($n^{25}D$ 1.4885), cyclohexyl,[13] heptyl, octyl ($n^{25}D$ 1.4930) and decyl. The refractive indices were determined on triple-distilled material. It has been our experience that the higher esters should be purified and stored under inert conditions since they darken rapidly when exposed to air and light at room temperatures.

Ethyl Nicotinate Methane-1,1-bis-(2-hydroxy-3-naphthoate).—Seven and seven-tenths grams (0.05 mole) of ethyl nicotinate was dissolved in 125 ml. of water containing 3.65 g. (0.1 mole) of hydrogen chloride. Twenty-two and one-tenth grams (0.05 mole, 95% pure) of sodium methane-1,1-bis-(2-hydroxy-3-naphthoate) was dissolved in 250 ml. of water and the solution was charcoaled and filtered. Both solutions were then simultaneously run into 100 ml. of water with stirring. A pale yellow precipitate formed immediately. Stirring was continued for one hour; then the precipitate was filtered and washed free of chloride ion with water. The pale yellow powder (22 g. = 81.5%) crystallized from dioxane in microcrystalline needles, m. p. 299–301° (dec.).

Anal. Calcd. for $C_{31}H_{25}NO_8$: N, 2.60. Found: N, 2.62.

Butyl Nicotinate Methane-1,1-bis-(2-hydroxy-3-naphthoate).—Following the same procedure as for the "methane" salt of ethyl nicotinate, 8.45 g. (0.05 mole) of butyl nicotinate, 3.65 g. (0.1 mole) of hydrogen chloride and 22.1 g. (0.05 mole, 95% pure) of sodium methane-1,1-bis-(2-hydroxy-3-naphthoate) gave 25.2 g. (93%) of pale yellow, microcrystalline powder, m. p. 292–294° (dec.).

Anal. Calcd. for $C_{33}H_{30}NO_8$: N, 2.46. Found: N, 2.32.

(7) All melting points and boiling points are uncorrected. The microanalyses were made by the Misses Esther Bass, Alice Rainey and Patricia Curran.

(8) Tergitol Penetrant 08, Carbide and Carbon Chemicals Corp., New York, N. Y.

(9) Strohbach, *Ber.*, **34**, 4162 (1901).

(10) Windaus and Kuhr, *Ann.*, **532**, 57 (1937).

(11) Crum and Robinson, *J. Chem. Soc.*, 561 (1943).

(12) Engler, *Ber.*, **27**, 1787 (1894); Hukosima, *J. Chem. Soc. Japan*, **61**, 121 (1940).

(13) Goldfarb, *J. Appl. Chem.* (*U. S. S. R.*), **10**, 515 (1937); *C. A.*, **31**, 6657 (1937).

Solubility Determinations.—The water solubilities[14] of the compounds listed in Table I were determined according to the following general method. An excess of the compound was put into a vessel and shaken with 150 cc. of water in a constant temperature bath overnight at 30°. The vessel was then taken out and shaken in another constant temperature bath for several hours at 25°. It is realized that these conditions do not necessarily ensure equilibrium, yet it was felt that the procedure was accurate enough for the purpose in question. Following this, an aliquot of the liquid was removed from the vessel with a pipet, the tip of which was protected by a piece of filter paper. The clear liquid was transferred quantitatively into a weighing bottle, which was then kept in a vacuum desiccator over calcium chloride at room temperature to remove most of the water. The samples were dried to constant weight at 60° *in vacuo*.

(14) The authors are grateful to Dr. G. W. Ewing of these laboratories for the determination of some of the water solubilities.

Summary

The preparation of water-insoluble, biologically active forms of thiamine and niacin for the enrichment of certain cereals is described.

The thiamine derivatives were obtained by interaction with various high molecular carboxylic and sulfonic acids; the latter also were used to obtain salts with alkyl nicotinates.

Water-insoluble derivatives of nicotinamide were prepared by interaction with *p*-aminobenzoic acid, phenyl isocyanate and 6-methoxy-8-aminoquinoline.

RENSSELAER, N. Y. RECEIVED NOVEMBER 8, 1945

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NEW JERSEY COLLEGE FOR WOMEN, RUTGERS UNIVERSITY]

Catalytic Alkylation of Chlorobenzenes

BY GERTRUDE VERMILLION AND MARTHA A. HILL[1]

The reversibility of the Friedel–Crafts reaction has been demonstrated by Boedtker and Halse.[2] By heating polyethyl- and polyisopropylbenzenes with benzene and a small quantity of aluminum chloride, they succeeded in recovering good yields of the corresponding monoalkylated compounds. Interconversion between mono- and polyalkylbenzenes with exchange of substituent groups, in the presence of aluminum chloride, has been reported more recently by Hoffmann, Farlow and Fuson[3] as additional proof of reversibility. This alkyl migration has been utilized by Reid and his associates to alkylate naphthalene by means of polyethylbenzene[4] and diisopropylbenzene.[5] Cline and Reid[6] have also employed a "transalkylation" method to prepare mono- from polyethylbenzene, with a high degree of conversion.

Alkyl transfer in the presence of anhydrous aluminum chloride occurs even when benzene is not added to the alkylated compound. Heise and Töhl[7] report the conversion of cumene at 100° to propane, benzene, diisopropylbenzene and tar. Near refluxing temperature, traces of toluene and substantial quantities of xylenes are produced, according to Moore and Egloff.[8]

In this investigation, the reaction of cumene with chlorobenzene, catalyzed by aluminum chloride, was studied as a new method of alkylating halobenzenes. Attempts to alkylate dichlorobenzenes by modifications of the same method were unsuccessful.

(1) This paper is taken from part of a thesis submitted to the Graduate Faculty of Rutgers University in partial fulfillment of the requirements for the degree of Master of Science.

(2) Boedtker and Halse, *Bull. soc. chim.*, **19**, 444 (1916).

(3) Hoffmann, Farlow and Fuson, THIS JOURNAL, **55**, 2000 (1933).

(4) Milligan and Reid, *ibid.*, **44**, 206 (1922).

(5) Berry and Reid, *ibid.*, **49**, 3142 (1927).

(6) Cline and Reid, *ibid.*, **49**, 3150 (1927).

(7) Heise and Töhl, *Ann.*, **270**, 155 (1892).

(8) Moore and Egloff, *Met. Chem. Eng.*, **17**, 61 (1917).

Experimental

Reagents.—Paragon cumene, of b. r. 150.0–151.5°[9] (758 mm.), $n^{20}D$ 1.4918, monochlorobenzene of b. r. 130.0–130.7° (759 mm.), $n^{20}D$ 1.5246, and sublimed aluminum chloride were used.

Procedure.—The catalyst was weighed into a one-liter, three-necked flask, to which the measured, liquid organic reagents were quickly added. A 360° thermometer, a mercury-sealed, motor-driven stirrer and a reflux condenser closed by a calcium chloride tube, were attached to the flask by silicone-lubricated, ground glass joints. All heating was done on a constant-level water-bath. At the end of the heating period the flask was cooled and the contents were poured into ice water (300 g. per 0.05 mole of aluminum chloride), with stirring to break up the complexes. The oily product was washed with 100 ml. of 5% sodium bicarbonate and 200 ml. of distilled water before drying over calcium chloride. The dried samples were fractionated through a 91-cm., vacuum-jacketed, Vigreux column.

In the preliminary run, 0.1 mole of aluminum chloride, 2 moles of cumene and 2 moles of chlorobenzene were taken. After an eight-hour reaction period at 90 ± 5°, the product consisted of 19% benzene, 6% high-boiling material, and 25% of an oil containing chlorocumene, with traces of diisopropylbenzene. Unreacted chlorobenzene, 36%, and 13% of unreacted cumene, were recovered.

Other experiments indicated that the conversion of chlorobenzene was increased by reducing the mole ratio of chlorobenzene to cumene, to 0.5:2. Reduction of temperature and reaction time caused lower yields, while an increase in catalyst concentration had no effect.

Cumene, alone, reacted in the presence of aluminum chloride yielding 18% benzene and 24% diisopropylbenzene in the oily top layer of product.

Identification of Products.—The fractions boiling below 83° were refractionated. The portion of b. r. 80.2–80.3° (762 mm.) was identified as benzene by its physical properties, d^{20} 0.8768 and $n^{20}D$ 1.5015.

A purified sample of diisopropylbenzene from the cumene digestion was found to have a b. r. of 195–197°, d^{20} 0.8580 and $n^{20}D$ 1.4897, checking the literature values.

Chlorocumene was isolated from the combined 188–196° distillation cuts. Three fractionations at 100 mm., followed by two at 11 mm., yielded a sample of b. r. 72-

(9) All boiling temperatures given in this paper are uncorrected