benzene solution. The yield of fine yellow needles was 1.1 g. (85%), m.p. 141–142°.

Anal. Calcd. for $C_{12}H_{11}N_3O_4$: N, 16.09. Found: N, 16.14.

5-Nitro-3-aminoquinoline. One gram (0.004 mole) of ethyl 5-nitro-3-quinolylurethan was refluxed with 50 ml. of 6N hydrochloric acid for 8 hr. and the volume reduced to one-half by distillation. The solution was allowed to cool on ice, after which the white solid was removed by filtration and the hydrochloride decomposed with sodium carbonate solution. The solid was collected, dried, and refluxed for 2 hr. with a solution of 9 ml. of acetic anhydride in 50 ml. of benzene. About one-half of the solvent was removed by distillation, the solution was cooled in ice water, and the solid was collected by filtration. The yield of crude 5-nitro-3-acetamidoquinoline was 1 g. (88%), m.p. 195–199°. The acetamido derivative was refluxed for one hour with 50 ml. of 20% hydrochloric acid and the solution was concentrated. When the solution cooled, the hydrochloride was collected by filtration. The substance was treated with sodium carbonate solution to liberate the amine which was recrystallized first from benzene, and then from water. The yield of bright red granular solid, m.p. 184.5–185° was 0.54 g. (70%).

Anal. Calcd. for $C_9H_7N_3O_2$: N, 22.22. Found: N, 22.22.

5-Nitro-3-acetamidoquinoline was purified by recrystallization from benzene. The substance melted at 202.5–203.5°.

Anal. Calcd. for $C_{11}H_9N_3O_3$: N, 18.18. Found: N, 18.14.

5-Nitro-3-phenylquinoline. 5-Nitro-3-aminoquinoline (1.1 g., 0.006 mole) was dissolved in 80 ml. of hot 28% hydrochloric acid. The solution was cooled rapidly to 0° and it was diazotized by the dropwise addition of 0.44 g. of sodium nitrite in 5 ml. of water. After the solution remained at 0° for a short time, 0.4 g. of urea was added. The cold diazonium salt solution was allowed to drip into a cold stirred solution of 10 ml. of 25% dimethylamine and 38 g. of sodium carbonate in 150 ml. of ice water. The temperature was held at 8–12°. After stirring for 30 min., the olive green solid was removed by filtration, washed, and dried in a vacuum. The yield of crude 1-(5-nitro-3-quinolyl)-3,3-dimethyltriazene, m.p. 103–105°, was 1.27 g. (90%).

A 200-ml. three-necked flask was fitted with a mechanical stirrer, dropping funnel, and a reflux condenser to which was attached a bubble counter. A solution of 1.27 g. of the dry crude triazene in 50 ml. of benzene was poured into the flask and the stirred solution was heated to boiling while 1.5 g. of toluenesulfonic acid in 30 ml. of benzene was added dropwise over a 20-min. period. The solution was refluxed until there seemed to be no further evolution of nitrogen. The benzene solution was washed with 100 ml. of 5% sodium hydroxide solution, then with water, and it was dried over sodium sulfate. After removal of the solvent, the residue was sublimed by heating it at 180° under 1–2 mm. pressure. A yield of 0.45 g. (35%) of pale yellow needles, m.p. 125–130°, was obtained. After a recrystallization from dilute ethyl alcohol and from hexane, the melting point was elevated to 156–156.5°.

Anal. Calcd. for $C_{15}H_{10}N_2O_2$: N, 11.20. Found: N, 11.56.

The *methiodide* was prepared by refluxing 5-nitro-3-phenylquinoline with methyl iodide and recrystallizing the substance from ethyl alcohol, m.p. 237–238°.

Anal. Calcd. for $C_{16}H_{13}IN_2O_2$: N, 7.14. Found: N, 7.07.

Nitration of 5-nitro-3-phenylquinoline. Nitration of 0.1 g. of this substance and isolation was carried out exactly like the procedure used for 3-(p-nitrophenyl)quinoline, using proportional amounts of reagents. A yield of 0.07 g. (58%) of product, m.p. 198–212°, was obtained. The substance was recrystallized from ethyl alcohol and from benzene–hexane to give fine yellow needles, m.p. 224.5–226°. A mixed melting point determination with the dinitro compound I showed no depression.

5-Chloro-3-(p-nitrophenyl)quinoline. Two-tenths gram of 5-chloro-3-phenylquinoline was nitrated and the product isolated by exactly the same procedure as for the previous nitrations. The crude nitration product was recrystallized from methanol–hexane solution and from absolute ethanol, giving slightly yellow needles, m.p. 183–184°. Oxidation of a sample yielded p-nitrobenzoic acid.

Anal. Calcd. for $C_{15}H_9ClN_2O_2$: Cl, 12.44. Found: Cl, 12.21.

The *methiodide* was obtained as fine yellow needles by refluxing 5-chloro-3-(p-nitrophenyl)quinoline with methyl iodide and recrystallization of the product from absolute ethanol, m.p. 247–249°.

Anal. Calcd. for $C_{16}H_{12}ClIN_2O_2$: N, 6.56. Found: N, 6.49.

BLOOMINGTON, IND.

Effect of Amines on Hydrogenolysis of Alkylphenols

WILLIAM H. CLINGMAN, JR., AND FRANCIS T. WADSWORTH

It has been demonstrated that the hydrogenolysis of alkyl phenols over nickel-on-kieselguhr catalyst can be inhibited by organic amines, although the latter do not prevent hydrogenation of the benzene ring. The data obtained support the hypothesis that both acidic sites and hydrogenation sites are present on the nickel catalyst.

In the hydrogenation of unsaturated alcohols with nickel catalysts both hydrogenation of the unsaturated double bonds and hydrogenolysis of the hydroxyl groups can occur. Recently Pines, *et al*[1] have proposed a carbonium ion mechanism for the hydrogenolysis reaction involving acidic sites on the catalyst. Pines reported that if the sites active for hydrogenation are poisoned with sulfur,

only hydrogenolysis occurs. If both pyridine and a sulfur-containing compound are present in the charge, no reaction occurs. According to Pines' hypothesis, the pyridine poisons the acidic catalyst sites responsible for hydrogenolysis.

In order to obtain further evidence for acidic sites in addition to hydrogenation sites on nickel catalysts, the effect of organic bases on the hydrogenolysis of the hydroxyl group in alkylphenols was studied. The hydrogenation of phenol and cresols with a nickel catalyst yields the correspond-

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(1) H. Pines, M. Shamaiengan, and W. S. Postl, *J. Am. Chem. Soc.*, **77**, 5099 (1955).

TABLE I

HYDROGENATION OF C_{15}-C_{18} ALKYLPHENOLS

Run No.	Alkyl-phenol, g.	n-Heptane, g.	Pyridine, g.	Catalyst[a]	Grams of Catalyst	Max. Temp., °C.	Max. H₂ Press., p.s.i.g.	Mole % Alcohol Yield Based on Alkylphenol Charged
83	200	200	0	Ni	140	218	1900	0
103	50	100	35	Ni	70	210	1500	49
24	46	70	0	Ni	70	249	1705	0
107	52	70	38	Ni	70	243	1500	92
95	100	100	0	Pt	45	256	1700	14
22	50	44	37	Pt	25	257	1440	35

[a] Ni is nickel-on-kieselguhr catalyst, Pt is 0.6% platinum on alumina.

ing cyclohexanols below 250°.[2,3] Secondary alcohols, however, undergo hydrogenolysis to hydrocarbons at 250° over a Raney nickel catalyst.[4] Thus, at and above 250°, the hydrogenation of phenol or the cresols gives hydrocarbons rather than alcohols as the main product.[2,3] In the present investigation the hydrogenations were carried out over nickel-on-kieselguhr catalysts using temperatures and catalyst concentrations at which hydrogenolysis occurred.

Several organic bases were found to be effective in preventing the hydrogenolysis of alkylphenols while not inhibiting the hydrogenation of the alkylphenol over nickel-on-kieselguhr catalyst. In the presence of pyridine, alkylphenols containing nine to twelve carbon atoms in the side chain can be readily hydrogenated to alkylcyclohexanol in high yields at 250°. In the absence of the organic base, such alkylphenols were completely reduced to hydrocarbons under the same conditions.

The yield of alkylcyclohexanol from various alkylphenols has been studied as a function of temperature and composition of the organic base. In almost all cases, the addition of an amine to the charge increased the yield over that obtained in the absence of the amine.

RESULTS AND DISCUSSION

In Table I are given the results for hydrogenation of a mixture of C_{15}-C_{18} alkylphenols both with and without pyridine added. Below 200°, even with large quantities of catalyst present, reaction of the alkylphenol with hydrogen was extremely slow. At 218° and above, complete reduction to alkylcyclohexanes took place in the absence of an organic base. That there were no hydroxyl groups in the product was verified by infrared spectroscopy.

The addition of pyridine to the charge, however,

(2) S. Ando, J. Soc. Chem. Ind. Japan, 34, Suppl. Binding, 320 (1931).

(3) P. Sabatiev and E. E. Reid, Catalysis in Organic Chemistry, D. Van Nostrand Co., New York, 1922, pp. 135, 166–7.

(4) B. Wojcik and H. Adkins, J. Am. Chem. Soc., 55, 1293 (1933).

inhibited hydrogenolysis of the hydroxyl group, a 92 mole % yield of alkylcyclohexanol being obtained at 243°. This result is consistent with the hypothesis of Pines[1] that an organic base poisons the acidic catalyst sites active for hydrogenolysis. It can also be seen from the results that the organic base was effective with both nickel and platinum catalysts.

In order to study further the effect of amines on the hydrogenolysis of alkylphenols, several runs were made with p-tert-butylphenol at different temperatures. Conclusions as to the effect of pyridine or triethylamine on the hydrogenolysis of the phenol could not be made because of a side reaction between the amine and phenol or its hydrogenation products. In every run in which either pyridine or triethylamine was added to the charge, there was produced a complex mixture of high molecular weight amines, which formed insoluble hydrogen chloride salts. No such products were formed, however, in the hydrogenation of the C_{15}-C_{18} alkylphenols in the presence of pyridine. It is, thus, likely that the p-tert-butylphenol or one of its hydrogenation products takes part in the reaction producing the high molecular weight amines. On this basis it would be expected that the addition of sufficient pyridine to the reactants would lower the alcohol yield (based on pheno charged) below that obtained with no amine present. This conclusion is supported by the data in Table II.

The high molecular weight amines formed from p-tert-butylphenol and either pyridine or triethylamine were found to consist of a mixture of primary, secondary, and tertiary amines. The acetamides of the high molecular weight secondary amines from the reaction of either pyridine or triethylamine had infrared spectra identical to each other. These acetamides had molecular weights somewhat higher than the molecular weight of the corresponding derivative of bis(tert-butylcyclohexyl) amine.

Several reactions of amines under hydrogenating conditions have been reported in the literature. Dicyclohexylamine is produced in yields of 75% or higher by hydrogenation of mixtures of aniline

TABLE II

HYDROGENATION OF p-tert-BUTYLPHENOL

Run No.	p-tert-Butyl-phenol, g.	n-Heptane, g.	Organic Base[a]	Organic Base, g.	Catalyst,[b] g.	Max. Temp., °C.	Max. H_2 Press., p.s.i.g.	Mole % Alcohol Yield Based on Alkylphenol Charged
27	80	36	—	0	70	182	1550	61
28	80	35	Pyd	17	70	177	1475	50
105	159	68	—	0	140	204	1700	36
10	80	35	TEA	16	70	204	1500	46
143	80	35	Pyd	17	70	207	1450	45
26	160	70	Pyd	81	140	207	1550	22
38	160	70	Pyd	80	140	212	1620	18
3	80	35	—	0	70	268	1500	2.1
137	80	34	Pyd	16	70	268	1500	5.7

[a] Pyd = Pyridine, TEA = Triethylamine. [b] Catalyst is nickel-on-kieselguhr.

TABLE III

EFFECT OF HIGH MOLECULAR WEIGHT AMINES ON THE HYDROGENATION OF p-tert-BUTYLPHENOL

Run No.	p-tert-Butyl-phenol, g.	n-Heptane, g.	Organic Base[a]	Organic Base, g.	Catalyst,[b] g.	Max. Temp., °C.	Max. H_2 Press., p.s.i.g.	Mole % Alcohol Yield Based on Alkylphenol Charged
10	80	35	TEA	16	70	204	1500	46
26	160	70	Pyd	81	140	207	1550	22
38	160	70	Pyd	80	140	212	1620	18
105	159	68	—	0	140	204	1700	36
14	80	95	a	90	70	204	1475	68
34	81	27	b	124	70	204	1500	68
37	80	13	b	62	70	207	1500	67
39	80	7	b	31	70	206	1570	66
27	80	36	—	0	70	182	1550	61
53	81	33	c	62	70	181	1500	82
63	80	35	—	0	70	157	1410	63
64	80	33	c	62	70	149	1500	90

[a] TEA = Triethylamine, Pyd = Pyridine, a = Product from Run 10, b = Product from Run 26, c = Product from Run 38. [b] Catalyst is nickel-on-kieselguhr.

and phenol over a Pd catalyst at 90–200°.[5] Sawa, et al.,[6] report that upon hydrogenating pyridine with nickel-on-kieselguhr catalyst in the presence of an alcohol, N-alkylpiperidine is formed. Thus, one probable tertiary amine from the reaction of p-tert-butylphenol with pyridine is N-(4-tert-butyl-cyclohexyl)piperidine.

In addition to the effect of pyridine on the hydrogenation of p-tert-butylphenol, the effect of temperature on the reaction may also be noted in Table II. As the temperature increases, the yield of alcohol, either in the presence or absence of organic base, decreases. This is to be expected since it is known that the extent of hydrogenolysis of alcohols increases with temperature.

In order to minimize condensation of p-tert-butylphenol with the amine, some experiments were made using samples of the mixture of amines that was produced in a previous reaction. This was

done by adding to the charge an aliquot of the total product from the previous reaction. The amount of alcohol thus introduced into the reactants was subtracted from the total amount of alcohol found after the hydrogenation in order to obtain the yield. The results of these experiments are reported in Table III. It can be seen that in every run in which the high molecular weight amine was added, a substantial increase in yield was obtained over the corresponding run with no amine added. The alcohol yield was also greater than that in the run in which the high molecular weight amine was produced.

It can be seen from Runs 34, 37, and 39 in Table III that the yield is not affected by the concentration of the complex amine mixture in the charge. If it is assumed that the high molecular weight amines poison acidic catalyst sites active for hydrogenolysis, then the alcohol yield should be independent of the amine concentration provided enough amine is present to poison these acidic sites. It again can be seen from Table III that lowering the hydrogenation temperature increases

(5) L. J. Dankert and D. A. Permoda (to Dow Chemical Co.), U. S. Patent 2,571,016 (October 9, 1951).

(6) Y. Sawa, K. Inone, and S. Kitamava, J. Pharm. Soc. Japan, 63, 319 (1943).

TABLE IV

HYDROGENATION OF CRESYLIC ACIDS

Run No.	Cresylic Acid, g.	n-Heptane, g.	Organic Base[a]	Organic Base, g.	Catalyst	Catalyst,[a] g.	Max. Temp., °C.	Max. H₂ Press., p.s.i.g.	Mole % Alcohol Yield Based on Alkylphenol Charged
54	51[b]	35	—	0	Ni-WS	80	273	1780	0
113	51[b]	34	Pyd	35	Ni-WS	83	268	1900	20
99	129[c]	70	Pyd	80	Ni	140	180	1880	60
86	51[c]	35	—	0	Ni	70	177	1500	54
100	50[c]	23	a	56	Ni	70	184	1775	75

[a] Ni = Nickel-on-kieselguhr, Ni-WS = Tungsten-nickel-sulfide, Pyd = Pyridine, a = Product from Run 99. [b] Acid oils recovered from catalytic cracking. [c] "215/225 Cresylic Acid" supplied by Merichem Co.

the yield both with and without organic base present. The highest yield obtained was 90% at 149° in the presence of the complex amine mixture.

The effect of amines on the yield was also investigated in the hydrogenation of cresylic acids over nickel-on-kieselguhr and tungsten-nickel-sulfide catalysts. From Table IV it can be seen that with the latter catalyst some yield improvement was obtained in the presence of pyridine. In Run 99 high molecular weight amines were produced from pyridine and cresylic acid under hydrogenation conditions. When these amines were added to the charge in Run 100, a 50% improvement was obtained over the alcohol yield of Run 86, in which no amine was added.

CONCLUSION

It has been found that organic bases inhibit the hydrogenolysis of alkylphenols over nickel-on-kieselguhr catalyst but do not poison the hydrogenating activity of this catalyst. This result is consistent with the hypothesis that acidic sites on the catalyst surface bring about the hydrogenolysis of hydroxyl groups and that these sites may be poisoned with amines. One would predict from this mechanism that the yield of alkylcyclohexanol would be independent of the concentration of the base, as long as enough amine was present to poison all of the acidic sites on the catalyst. This prediction is also in agreement with the experimental results.

It can be concluded from the data presented that the beneficial effect of the amine on the yield is greater the higher the molecular weight of the alkylphenol. This trend is expected since hydrogenolysis, which the amine inhibits, is more extensive with the higher molecular weight phenols. It was also found that the lower the temperature, the higher the alcohol yields obtained from p-tert-butylphenol both with and without added amine.

EXPERIMENTAL

Materials. The C₁₅–C₁₈ alkylphenols used were prepared by the BF₃-catalyzed addition to phenol of C₉–C₁₂ polypro-

pylene olefins with an average molecular weight of 139, and boiling range of 153–200°. These alkylphenols contained 4.5 meq. of hydroxyl groups per gram, while phenol itself contains 10.6 meg. of hydroxyl groups per gram. p-tert-Butylphenol was obtained from Eastman Kodak Co., and the purity was 98% as determined from the hydroxyl number. The Merichem Co. supplied the cresylic acid, which contained mainly xylenols and had a sulfur content of 0.04%. Phillip's pure grade n-heptane, c.p. pyridine, and Eastman triethylamine were also used.

The nickel-on-kieselguhr catalyst contained 65–70% nickel and was supplied by the Harshaw Chemical Co., while the tungsten-nickel-sulfide catalyst was obtained from the Shell Oil Co.

Hydrogenation procedure. All of the hydrogenation runs were conducted in a similar manner, and the procedure will be given for a typical example (Run 143). p-tert-Butylphenol (80.0 g.), n-heptane (35.3 g.), and pyridine (17.4 g.) were charged to an Aminco 1400-ml. stainless steel, high pressure bomb. Nickel-on-kieselguhr catalyst (70 g.) was reduced in a hydrogen stream for 1 hr. at 260–315° and then added to the charge. Hydrogen was pressured into the reactor up to 1,000 p.s.i.g., heat supplied by electrical heaters, and the reactants agitated for 5 hr. after the reaction temperature of 204° had been reached. Hydrogen was added intermittently to keep the pressure between 1000 and 1450 p.s.i.g.

After cooling, the reactants were rinsed from the bomb with n-heptane and the catalyst filtered from the solution. In order to remove the complex mixture of amines formed during the reaction, 100 ml. of 1:1 HCl was added. The white solid which formed was filtered off and digested with n-heptane on a steam bath to dissolve the small amount of tert-butylcyclohexanol present. The n-heptane solutions so obtained were twice washed with 100 ml. of 5% NaOH. After drying over Na₂SO₄, the alcohol yield was determined by acetylation with acetic anhydride. In the case of the cresylic acids, the product was analyzed directly for hydroxyl groups without washing or prior removal of amines because of the partial solubility of the alkylcyclohexanols in water. The yield was determined by acetylating the products with acetic anhydride and correcting the results for the high molecular weight amines present. The products also were tested for unreacted alkylphenol with FeCl₃. In all runs reported in Table IV, the product contained less than 0.1% of the original phenolic compound.

Hydrogenation products. In order to characterize the compounds formed in a typical hydrogenation of p-tert-butylphenol, the product from Run 27 (Table II) was distilled and each of the fractions analyzed by infrared spectroscopy. The only products found were 4-tert-butylcyclohexanol (64 wt. %), tert-butylcyclohexane (14 wt. %), and an unknown compound or mixture boiling in the same range as the

alcohol (10 wt. %). This unknown compound was probably a condensation product from p-tert-butylphenol, but the infrared spectrum of this fraction showed no bands due to functional groups other than the hydroxyl group in tert-butylcyclohexanol. This alcohol was characterized by preparing its phenylurethan derivative (m.p. 161–163°). One conclusion that can be drawn from the data is that the tertiary butyl group was not cleaved from the ring during

hydrogenation since neither cyclohexane nor cyclohexanol was found in the products.

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TEXAS CITY, TEX.

Convenient Syntheses of p-Bromo- and p-Aminophenol

H. E. PODALL AND W. E. FOSTER

Convenient syntheses are described for preparing p-bromophenol in high yield and high purity and for p-aminophenol in high yield. Possible mechanisms for the copper sulfate-catalyzed ammonolysis of p-halophenols are discussed.

While investigating the synthesis of p-aminophenol from phenol *via* p-bromophenol, several interesting observations were made. It was found that the bromination of phenol by the *Organic Syntheses* procedure,[1] using equimolecular amounts of phenol and bromine in ethylene dichloride instead of carbon disulfide, gave an 83% yield of crude p-bromophenol containing as much as 12% 2,4-dibromophenol.[2] Variations in the rate of addition of the bromine solution, stirring, dilution, temperature (−5 to +5°), or dryness of the ethylene dichloride solvent gave little or no improvement in the conversion beyond 72% pure p-bromophenol. However, use of a 20% or greater excess of phenol resulted in a substantial decrease in the amount of 2,4-dibromophenol and a corresponding increase in the conversion and purity of p-bromophenol. The procedure developed here was found to be very convenient not only because of the high conversion to p-bromophenol but because of the ease of obtaining high purity p-bromophenol.

It is of interest to note that there was a direct correlation between the amount of 2,4-dibromophenol and the amount of unreacted phenol in the experiments where equimolecular amounts of phenol and bromine were used. Moreover, the ortho and meta isomers were in every case present to the extent of less than 1–2% and showed no variation with the amount of 2,4-dibromophenol formed. This indicates that the 2,4-dibromophenol was formed almost exclusively from p-bromophenol.

Although the aminolysis of p-bromophenol with methylamine has been reported,[3] the corresponding

reaction with ammonia apparently has not been. References were found, however, to the ammonolysis of p-chlorophenol. In one reference[4] the conditions given involved reaction at 140° for 12 hr. in the presence of catalytic amounts of copper sulfate (no yield given), whereas in the other reference[5] the optimum conditions involved reaction of one volume p-chlorophenol with 4 volumes of 33% aqueous ammonia containing 16% copper sulfate at 185° for 3 hr. to produce an 82% yield of p-aminophenol. Since p-bromophenol reacts much more readily with methylamine than does p-chlorophenol, it appeared that considerably milder ammonolysis conditions could be used for the p-bromophenol than those reported for p-chlorophenol.

The initial ammonolysis experiments with p-bromophenol were therefore conducted in the presence of catalytic amounts of copper sulfate at 25° to 60°. It was found that no significant reaction occurred. Consequently, it appears that there is a considerable difference in the reactivity of ammonia and methylamine towards p-halophenols, possibly even more than would correspond to their relative basicities (which differ by a factor of about 30). Some experiments were then conducted in the presence of relatively large quantities of copper sulfate (0.34 mole per mole p-bromophenol) as specified in one of the references for the ammonolysis of p-chlorophenol. At 65 to 140° the conversion to p-aminophenol was at best only 39%, and at 140° appreciable tar formation also occurred. Use of milder conditions in the presence of catalytic amounts of copper sulfate was therefore indicated.

A reaction variable study gave the following results: (*1*) The yield of p-aminophenol from p-bromophenol increased appreciably from 25° to 120° and

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(1) R. Adams and C. S. Marvel, *Org. Syntheses*, **Coll. Vol. I**, 128, (1941).

(2) 2,4-Dibromophenol and p-bromophenol boil within one degree at the distillation pressures used. The components were determined by infrared analyses.

(3) F. R. Bean (to Eastman Kodak) U. S. Patent **2,397,-911**, Apr. 9, 1946.

(4) German Patent **205,415**, Dec. 31, 1907. Akt.-Ges. fur Anilin-Fabrikation, Berlin.

(5) A. I. Kipriyanov, G. I. Kipriyanov, and M. Dashevskii, *Ukrain. Khem. Zhur.*, **7** Wiss. Tech. Abt. 87–93 (1932).