hydroxide and with water, the organic layer was separated and fractionated. There was obtained 58 g. (44% theory) of *N*-ethyl-2-ethylaniline (b.p. 117–117.5° at 20 mm., n_D^{20} 1.5398). The benzoyl derivative (m.p. 46.5–48°) and the 3-nitrobenzenesulfonyl derivative (m.p. 116–117°) of this compound were prepared. The mixed melting points of these derivatives with the corresponding ones of the ethylation product of *N*-ethyl-aniline were not depressed.

Synthesis of N-ethyl-2-ethyl-5-chloroaniline. The following synthesis of *N*-ethyl-2-ethyl-5-chloroaniline was carried out to elucidate the structure of the products from the ethylation of *N*-ethyl-3-chloroaniline.

Nitration of 1-chloro-4-ethylbenzene. Fractionation of practical grade 1-chloro-4-ethylbenzene (Distillation Products Industries) through a 60-plate column yielded the pure isomer (b.p. 182°; n_D^{20} 1.5174).[10] Nitration of this material was effected in two batches. In the first reaction 281 g. (2.0 moles) of 1-chloro-4-ethylbenzene was dispersed in 500 g. of 80% (wt.) sulfuric acid and maintained at 35–40° while a solution of 187 g. of concentrated nitric acid in 460 g. of concentrated sulfuric acid was added over a 35-min. period. The mixture was then heated to 90° and maintained at that temperature for 30 min. After cooling, the product was poured over ice and the organic layer separated. A second nitration was carried out using 369 g. (2.63 moles) of 1-chloro-4-ethylbenzene and proportional amounts of acid, and the product combined with that of the first nitration. After washing with water and with 10% sodium carbonate solution, the product was dried and distilled through a 20-plate column to yield 624 g. (73% theory) of mononitrated product (b.p. 144–160° at 29 mm.). Refractionation through a 60-plate column resulted in the separation of two isomers. There was obtained 286 g. of a low boiling isomer, I, (b.p. 147° at 30 mm.; n_D^{20} 1.5518) and 292 g. of a high boiling isomer, II, (b.p. 162° at 30 mm.; n_D^{20} 1.5499).

Oxidation of I in basic solution with potassium permanganate showed it to be 2-nitro-4-chloroethylbenzene in that the product was 2-nitro-4-chlorobenzoic acid, m.p. 141–142° (lit. m.p. 140–141°).[11] Similarly II was shown to be 3-nitro-4-chloroethylbenzene by oxidation to 3-nitro-4-chlorobenzoic acid, m.p. 180–181.5°, (lit. m.p. 180°).[12]

Reduction of 2-nitro-4-chloroethylbenzene. A total of 216 g. (1.16 moles) of I was reduced in two batches with stannous chloride following the procedure employed by Gray and Bonner for the reduction of 4-methoxy-3-nitroacetophenone.[13] After freeing the amine by treating the reaction product with sodium hydroxide, the product was separated, dried, and fractionated to yield 150 g. (83%) of 2-ethyl-5-chloroaniline (b.p. 155° at 33 mm.; n_D^{20} 1.5742).

Acetylation of 2-ethyl-5-chloroaniline. A 128 g. (0.83 mole) portion of 2-ethyl-5-chloroaniline was treated with 93 g. (0.91 mole) of acetic anhydride and the product recrystallized from ethanol to yield 115 g. (70% theory) of 2-ethyl-5-chloroacetanilide (m.p. 140–141°).

Anal. Calcd. for $C_{10}H_{12}ClNO$: C, 60.76; H, 6.12. Found: C, 61.2; H, 5.97.

Reduction of 2-ethyl-5-chloroacetanilide. A solution of 11.4 g. (0.3 mole) of lithium aluminum hydride in 1200 ml. of ether was heated to boiling and the reflux from a Soxhlet extractor used for the addition of 79 g. (0.4 mole) of 2-ethyl-5-chloroacetanilide. The product was hydrolyzed by the addition of water and the product separated by ether and benzene extractions. Fractionation of the combined extracts yielded 41 g. (56% theory) of *N*-ethyl-2-ethyl-5-chloroaniline (b.p. 127° at 26 mm.; n_D^{20} 1.5552). There was also obtained 12 g. of unreduced 2-ethyl-5-chloroacetanilide. The infrared spectrum of this material was identical with that of the higher boiling isomer from the ethylation of *N*-ethyl-3-chloroaniline. Further proof of the identity was obtained by the preparation of the hydrochloride of the synthesis product (m.p. 115–116°) and determining mixed melting points with the hydrochlorides of the two isomeric ethylation products, (Table III). The mixed melting point with the hydrochloride of the high boiling isomer was undepressed (115–116°) while that of the hydrochloride of the low boiling isomer was depressed (93–110°). It is thus apparent that the high boiling isomer is *N*-ethyl-2-ethyl-5-chloroaniline, and by inference the low boiling isomer must be *N*-ethyl-2-ethyl-3-chloroaniline.

Acknowledgment. The authors wish to express their appreciation to Dr. Rex D. Closson for helpful suggestions in the undertaking of this investigation.

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(10) Martin, *Ind. Eng. Chem.*, **41**, 2876 (1949) has reported 1-chloro-4-ethylbenzene to boil at 184.42° (Corr.) and to have a refractive index n_D^{20} 1.5175.

(11) Green and Lawson, *J. Chem. Soc.*, **59**, 1019 (1891).

(12) King and Murch, *J. Chem. Soc.*, **127**, 2646 (1925).

(13) Gray and Bonner, *J. Am. Chem. Soc.*, **70**, 1251 (1948).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ETHYL CORPORATION]

The *ortho*-Alkylation of Phenols[1]

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The reaction of phenols with olefins in the presence of aluminum phenoxide-type catalysts has been investigated and under proper reaction conditions found capable of yielding predominantly 2-alkyl and 2,6-dialkylphenols. The mechanism of the reaction is discussed.

The alkylation of phenols has been conducted with a variety of catalysts and alkylating agents.[3] In the majority of cases *para*-alkylation was the predominant mode of reaction. The preparation of 2,6-dialkylphenols by direct alkylation was found to be difficult. Unless the *para* position was blocked, very little, and in some instances, no 2,6-dialkylphenols were obtained. To prepare 2,6-dialkylphenols multistep syntheses have been used. Thus 2,6-di-*tert*-butylphenol had been prepared only by the

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(1) Presented in part before the Division of Organic Chemistry at the 130th meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1956 and in a preliminary Communication, *J. Org. Chem.*, 21, 712 (1956).

(2) Present address, Koppers Co., Inc., Koppers Bldg., Pittsburgh, Pa.

(3) Price, *Org. Reactions*, III, 58 (1946).

TABLE I

COMPOSITION OF PHENOL-ISOBUTYLENE ALKYLATION PRODUCTS (MOLE PERCENT)

Experiment No.	1	2	3	4	5
Reaction temperature (°C.)	65–68	105–115	115–168	300–320	150–190
Length of run (hr.)	3	3.5	1.3	0.8	4
Isobutylene pressure (p.s.i.)	0–95	30–100	50–200	180–360	Atm.
Phenol	27	5	7	46	71
Phenyl *tert*-butyl ether	12	—	—	—	—
2-*tert*-Butylphenol	43	46	52	7	—
4-*tert*-Butylphenol	1	1	2	33	14
2,6-Di-*tert*-butylphenol	5	36	12	—	—
2,4-Di-*tert*-butylphenol	2	5	15	3	—
2,4,6-Tri-*tert*-butylphenol	—	6	6	2	—

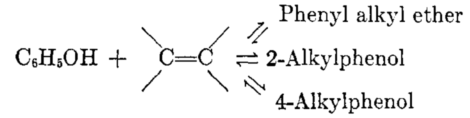
alkylation of the para-halophenol followed by removal of the para-halogen.[4] This paper describes the use of a new type of catalyst, the aluminum phenoxides, with which phenolic compounds may be directly alkylated with olefins to yield products containing a high percentage of 2-alkyl- and 2,6-dialkylphenols. Minor amounts of the ethers of phenol and of 2-alkylphenol were obtained in the products of those runs carried out at minimum reaction temperatures.

When phenol was alkylated with ethylene or propylene in the presence of aluminum phenoxide, no 4-alkylphenol was detected in any product under the reaction conditions used in the investigation. However, when isobutylene was used as the alkylating agent, the variation of product composition with changes in reaction variables became much more significant. Here again it was found that some ether production resulted from low temperature operation (Table I, Exp. 1). A much more serious complication was the appearance of *para*-substituted phenols in the products of the runs at higher temperatures. The extreme case was that of a reaction carried out at atmospheric pressure and relatively high temperatures (Table I, Exp. 5) in which 4-*tert*-butylphenol was the only alkylation product.

Under suitable reaction conditions, aluminum phenoxide catalyst was found to be highly selective even when isobutylene was used as the olefinic reactant; the alkylation of phenol with this olefin gave a 74% yield of 2,6-di-*tert*-butylphenol. Since the olefin feed system used differed from those used in the other experiments, this result is not included in Table I, but may be found under Experimental.

A group of simple dealkylation experiments was carried out to determine the cause of the variation in product composition. It was found that phenyl *tert*-butyl ether as well as both the 2- and the 4-*tert*-butylphenols were stable at their normal boiling points in the absence of catalyst. However, in the presence of aluminum phenoxide the ether is readily dealkylated at 100°, 2-*tert*-butylphenol is rapidly dealkylated at 190°, but 4-*tert*-butylphenol is stable even at its boiling point (236°). From these experiments, the factors controlling product composition are apparent.

The specificity of the reaction is the result of the rates and equilibria of a group of competing reactions.



To account for the formation of predominantly ether and *ortho*-alkylphenols, the rate of formation of these compounds must be much faster than the rate of formation of the *para*-isomer. However, these compounds are not thermodynamically the most stable products, at least at elevated temperatures, and it is necessary that the reaction be stopped before equilibrium is attained or else *para*-substituted products may be expected to predominate. Thus it is obvious that the experiment carried out at atmospheric pressure and high temperatures would promote the reverse reactions of the unstable products by simple mass action principle. Conversely, a reaction carried out at relatively low temperature, with high olefin concentration, and with an optimum reaction time should achieve maximum *ortho*-isomer concentration; these were the conditions used to effect a 74% conversion to 2,6-di-*tert*-butylphenol.

It is of interest to give some consideration to the mechanism of the aluminum phenoxide catalyzed reaction. The reactivity of different types of olefins in the reaction is typical of carbonium ion type reactions ($R_2C{=}CH_2 > RCH{=}CH_2$ or $RCH{=}CHR > CH_2{=}CH_2$). The elegant investigation of the aluminum alkoxides by Meerwein and Bersin[5] has shown that such compounds tend to coordinate with a molecule of alcohol to form acid solutions which may be titrated with alcoholic sodium alkoxide to the thymophthalein end point and the formation of a salt, $NaAl(OR)_4$. Although the acid, $HAl(OR)_4$ could not be isolated except as its metal salts, there is no reason to doubt its existence. Such behavior is analogous to that of the aluminim hal-

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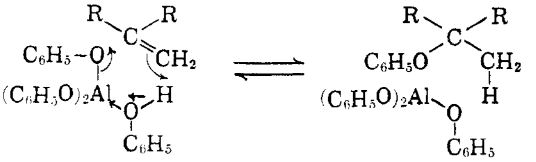
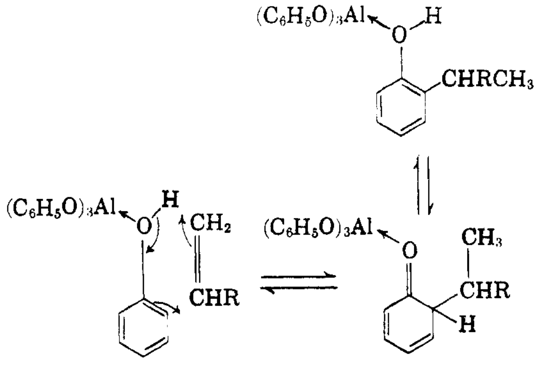
(4) Stillson and Sawyer, U. S. Patent **2,459,597** (January 18, 1949); Hart and Cassis, *J. Am. Chem. Soc.*, **73**, 3179 (1951).

(5) Meerwein and Bersin, *Ann.*, **476**, 113 (1929).

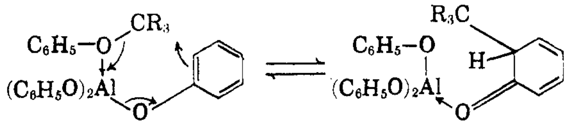
ides. The role of halogen acids and aluminum halides in forming σ complexes with aromatic hydrocarbons[6] and of alkyl halide-aluminum halide complexes in Friedel-Crafts alkylations of aromatic hydrocarbons[7] illustrates the tendency of aluminum halides to participate in AlX_4^- complexes. It might then reasonably be assumed that as a derivative of an acid of intermediate strength, aluminum phenoxide would exhibit properties intermediate to those of the aluminum alkoxides and the aluminum halides. As such it might be expected to complex with a molecule of phenol to give an acid, $HAl(OC_6H_5)_4$.



Ether formation.



Direct *ortho*-alkylation



Ortho-Alkylation *via* ether

Such a complex possesses a geometry ideally suited for reaction with olefins in several six-membered ring concerted mechanisms. There is also the interesting question as to whether the aromatic rings in such a complex are activated or deactivated. In any case it must be kept in mind that the thermodynamics of the reaction are not altered, and the success of aluminum phenoxide as an *ortho*-alkylation catalyst must be attributed both to its selectivity for *ortho*-alkylation and its moderate catalytic activity, which permits the accumulation of the unstable *ortho*-alkylation products.

EXPERIMENTAL[8]

Alkylation of phenol with ethylene. The aluminum phenoxide catalyst was prepared by adding 4.5 g. ($^1/_6$ formula wt.) of aluminum turnings in small amounts and with vigorous stirring to 300 g. of phenol at 165° under a nitrogen atmosphere. When hydrogen evolution had ceased, the mixture was cooled and transferred along with an additional 300 g. of phenol to a 2-l. steel autoclave. The catalyst preparation and the transfer process were carried out under a nitrogen atmosphere to protect the material from oxygen and moisture. The stirrer was started and the autoclave heated to 200° at which point ethylene was added to give 500 p.s.i. total pressure. Heating was resumed, and when the temperature reached 280° a drop in pressure was noted. More ethylene was then added to raise the pressure to 800 p.s.i. and the pressure maintained at 600 to 800 p.s.i. by repressuring when necessary. The temperature was maintained between 280° and 320° and a 2100-p.s.i. pressure drop noted over a 10-hr. period. After cooling, the product was removed from the autoclave and shaken with 200 ml. of 5% hydrochloric acid. The mixture was filtered prior to removing the aqueous phase. After washing twice with water, toluene was added and the product dried by azeotropic distillation. The product was fractionally distilled to yield 259 g. (43%) of recovered phenol, 189 g. (24%) of 2-ethylphenol, 79 g. (8%) of 2,6-diethylphenol and 63 g. of higher boiling material.

About 8 g. (1%) of phenyl ethyl ether was also obtained as a caustic insoluble material from the fraction boiling below phenol. Identification was based upon its physical properties (m.p. −31 to −30°, b.p. 165–167°, n_D^{20} 1.5066). The 2-ethylphenol boiled at 201–202° and had a refractive index (n_D^{20}) of 1.5372.

Anal. Calcd. for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.3; H, 8.11.

The aryloxyacetic acid derivative of the 2-ethylphenol was prepared and found to melt at 138–140° (lit. m.p. 140–141°).[9]

The 2,6-diethylphenol boiled at 219° and after recrystallization from hexanes melted at 37–38° (lit. m.p. 37.5–38°).[10]

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 79.4; H, 9.22.

The phenyl urethan of 2,6-diethylphenol was prepared and upon recrystallization from benzene found to melt at 170–171°.

Anal. Calcd. for $C_{17}H_{19}NO_2$: N, 5.20. Found: N, 5.31.

The aryloxyacetic acid derivative of 2,6-diethylphenol, recrystallized from isooctane, melted at 67–68°.

Anal. Calcd. for $C_{12}H_{16}O_3$: Neut. Equiv., 208. Found: neut. equiv., 204.

Alkylation of phenol with propylene. The autoclave was charged with a phenol-aluminum phenoxide mixture prepared from 565 g. (6 moles) of phenol and 4.5 g. ($^1/_6$ formula wt.) of aluminum turnings as in the above experiment. Propylene was charged to the autoclave as required from a specially constructed heated propylene supply cylinder. Alkylation was effected at 240° over a 2-hr. period using incremental propylene addition at 200 to 500 p.s.i. The product was processed as in the above ethylation to yield 656 g. (61%) of 2,6-diisopropylphenol (m.p. 19°, b.p. 136° at 30 mm., n_D^{20} 1.5139, d_4^{20} 0.955).

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.8; H, 10.2.

Proof of structure of 2,6-diisopropylphenol. A solution of 35 g. (0.2 mole) of 2,6-diisopropylphenol, 34 g. (0.25 mole) of sulfuryl chloride, and one drop of pyridine was warmed slightly whereupon a vigorous evolution of gas resulted.

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(6) Brown and Pearsall, *J. Am. Chem. Soc.*, **74**, 191 (1952).

(7) Brown and Grayson, *J. Am. Chem. Soc.*, **75**, 6285 (1953); Brown and Wallace, *J. Am. Chem. Soc.*, **75**, 6279 (1953).

(8) All melting points and boiling points are uncorrected.

(9) Steinkopf and Hopner, *J. prakt. Chem.* [2], **113**, 140 (1926).

(10) von Auwers and Wittig, *Ber.*, **57**, 1275 (1924).

The mixture was heated to 100° to insure complete reaction. Fractionation of the product yielded 24 g. (56%) of 2,6-diisopropyl-4-chlorophenol (b.p. 152–153° at 17 mm., n_{D}^{20} 1.5291).

Anal. Calcd. for $C_{12}H_{17}OCl$: Cl, 16.7. Found: Cl, 16.9.

The infrared spectrum of this material was identical with that of the 2,6-diisopropyl-4-chlorophenol obtained in the following experiment.

Alkylation of 4-chlorophenol with propylene. The catalyst was prepared by heating 386 g. (3 moles) of 4-chlorophenol and 100 ml. of toluene with 2.25 g. ($^1/_{12}$ formula wt.) of aluminum turnings. Alkylation with propylene was effected at 160 to 170° and 200 to 600 p.s.i. over a 2.5-hr. period. The product yielded 291 g. (46%) of 2,6-diisopropyl-4-chlorophenol (b.p. 165–166.5° at 30 mm., n_{D}^{20} 1.5285).

Alkylation of phenol with isobutylene. A series of four reactions was carried out to demonstrate the effect of alkylation temperature upon product composition in this reaction (Table I, Exp. No. 1-4). These runs were carried out using the same molar quantities of phenol and catalyst and the gaseous olefin feed system as employed in the alkylation of phenol with propylene. In a fifth experiment (Table I, Exp. No. 5) the catalyst concentration was doubled and the experiment was carried out at atmospheric pressure in glass apparatus.

Phenyl *tert*-butyl ether was separated as the caustic insoluble portion of a fraction boiling below phenol in the fractionation of the product from Experiment No. 1. Upon redistillation, the pure ether was obtained (m.p. −24 to −25°, b.p. 90° at 32 mm., n_{D}^{20} 1.4881). Stevens[11] has reported a similar boiling point of 80° at 20 mm. for this compound.

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 80.1; H, 9.33.

The physical properties of the phenolic compounds obtained in the reaction are presented in Table II. The values are in good agreement with those in the literature.[12]

TABLE II

PHYSICAL PROPERTIES OF PHENOL-ISOBUTYLENE REACTION PRODUCTS

Compound	M.P. (°C.)	B.P. (°C. at 30 mm.)
2-*tert*-Butylphenol[a]	−6.8[b]	120
4-*tert*-Butylphenol	99	138
2,6-Di-*tert*-butylphenol	36.5	147
2,4-Di-*tert*-butylphenol	57	156
2,4,6-Tri-*tert*-butylphenol	130	—

[a] n_{D}^{20} 1.5239, d_{4}^{20} 0.982. [b] An allotropic form melts at −19.2°.

Alkylation of phenol with isobutylene (optimum conditions). This experiment was carried out in an attempt to obtain a high conversion to 2,6-di-*tert*-butylphenol. The catalyst was prepared by heating 376 g. (4 moles) of anhydrous phenol and 100 ml. of toluene with 3.6 g. (0.13 formula wt.) of aluminum turnings. In this experiment the heated isobutylene feed cylinder was replaced by a weighed cylinder from which liquid isobutylene could be forced into the autoclave as desired by nitrogen pressure.

The phenol and catalyst mixture was heated to 100°. At this point 425 g. (7.6 moles) of liquid isobutylene was fed to the autoclave as rapidly as possible with sufficient cooling available to control the initial exothermic reaction. After the olefin addition was complete, the mixture was maintained at 100° to complete the reaction. The pressure in the autoclave passed through a maximum of 240 p.s.i. and finally dropped to 115 p.s.i. It is suspected that about 100 p.s.i. of the final pressure may be attributed to nitrogen dissolved in the isobutylene. The total reaction time was 7 hr. The product was processed as in the above experiments to yield 3% of recovered phenol, 9% of 2-*tert*-butylphenol, 74% of 2,6-di-*tert*-butylphenol and 9% of 2,4,6-tri-*tert*-butylphenol.

Alkylation of phenol with cyclohexene. The catalyst was prepared by heating 300 g. (3.2 moles) of phenol with 2.25 g. ($^1/_{12}$ formula wt.) of aluminum turnings. The mixture was cooled and 232 g. (3.0 moles) of cyclohexene added. The autoclave was then heated to 244° at which point an exothermic reaction was apparent and the pressure dropped from 140 to 40 p.s.i. The product was worked up to yield 83 g. (29%) of phenol, 236 g. (42%) of 2-cyclohexylphenol, 6 g. (1%) of 4-cyclohexylphenol, and 170 g. (20%) of 2,6-dicyclohexylphenol.

The 2-cyclohexylphenol (m.p. 55.5–57°, b.p. 173° at 30 mm.) gave no depression of melting point when mixed with an authentic sample of that compound. The 2,6-dicyclohexylphenol (b.p. 190° at 30 mm.) melted at 62–63.5° after recrystallization from isooctane (lit. m.p. 62–65°).[13]

Alkylation of phenol with 1-decene. The catalyst mixture was prepared from 300 g. (3.2 moles) of phenol and 4.5 g. ($^1/_6$ formula wt.) of aluminum turnings in the usual manner. The mixture was heated in the autoclave with 167 g. (1.28 moles) of 1-decene until a temperature of 300° was reached in the course of a 90-min. period. No exothermic reaction or drop in pressure was noted. The product was treated in the usual manner to yield 138 g. (49%) of "2-(2-decyl)phenol," b.p. 198–200.5° at 30 mm., n_{D}^{20} 1.5010. The infrared spectrum showed the presence of the hydroxyl band.

Anal. Calcd. for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 82.1; H, 11.3.

Alkylation of phenol with diisobutylene. The catalyst was prepared by heating 234 g. (2.38 moles) of phenol with 4.5 g. ($^1/_6$ formula wt.) of aluminum turnings and 252 g. (2.42 moles) of diisobutylene, added after cooling. The mixture was heated to 280° over a 90-min. period with no evidence of reaction. Upon cooling, the reactor showed no residual pressure (indicating the absence of isobutylene), and distillation of the product indicated that no *tert*-butyl phenols were present. From the product was obtained 89 g. (40%) of phenol, 55 g. (11%) of 2-(1,1,3,3-tetramethylbutyl) phenol, 123 g. (25%) of 4-(1,1,3,3-tetramethylbutyl)phenol and 60 g. of higher boiling material. The *ortho*-isomer melted at 43–44° and boiled at 157–158.5° (30 mm.).

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.49; H, 10.75. Found: C, 81.4; H, 10.7.

The *para*-isomer melted at 85–86° (lit. m.p. 84°)[10] and boiled at 175° (30 mm.). The infrared spectra of both isomers showed the presence of the hydroxyl group.

Alkylation of 1-naphthol with propylene. The autoclave was charged with 502 g. (3.48 moles) of 1-naphthol and 2.25 g. ($^1/_{12}$ formula wt.) of aluminum turnings and an unsuccessful attempt was made to prepare the catalyst by heating to 329°. The autoclave was then cooled and 17 g. ($^1/_{12}$ mole) of aluminum isopropoxide added. The mixture was heated to 300–310° and alkylated with propylene at 600 to 700 p.s.i. over a 3-hr. period. The catalyst was hydrolyzed and removed before performing a preliminary distillation through a Vigreux column to yield 98 g. (20%) of 1-naphthol (b.p. 140–160° at 10 mm.), 374 g. of crude 2-isopropyl-1-naphthol (b.p. 160–190° at 10 mm.), and 51 g. of higher boiling materials. Refractionation of the crude 2-isopropyl-1-naphthol through a 30-plate column gave 345 g. (54%) of purified material (m.p. 45–50°, b.p. 192.5–193.5° at 30 mm.). Recrystallization from isooctane raised the melting point to 49–50°, and this material showed no melting point depression when mixed with an authentic sample[14] of 2-isopropyl-1-naphthol.

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(11) Stevens, *J. Org. Chem.*, **20**, 1233 (1955).

(12) Pardee and Weinrich, *Ind. Eng. Chem.*, **36**, 596 (1944).

(13) Skraup and Beifuss, *Ber.*, **60**, 1070 (1927).

(14) Ecke and Napolitano, *J. Am. Chem. Soc.*, **77**, 6373 (1955).

Anal. Calcd. for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.7; H, 7.59.

Alkylation of 2-chlorophenol with isobutylene. The catalyst was prepared in the autoclave by heating 644 g. (5 moles) of 2-chlorophenol with 4.5 g. ($^1/_6$ formula wt.) of aluminum turnings. Alkylation with isobutylene was effected at 80–90° and the product worked up to give 550 g. (60%) of 2-*tert*-butyl-6-chlorophenol (b.p. 123° at 30 mm.; n_D^{20} 1.5265).

Anal. Calcd. for $C_{10}H_{13}ClO$: Cl, 19.2. Found: Cl, 19.3.

Proof of structure of 2-tert-butyl-6-chlorophenol. A portion of the product of the above experiment was chlorinated with sulfuryl chloride to yield 2,4-dichloro-6-*tert*-butylphenol (for chlorination method see under structure proof of 2,6-diisopropylphenol). The 2,4-dichloro-6-*tert*-butylphenol was obtained in 54% yield (b.p. 134° at 15 mm., n_D^{20} 1.5421).

Anal. Calcd. for $C_{10}H_{12}Cl_2O$: Cl, 32.3. Found: Cl, 32.4.

This material had physical properties and infrared spectrum identical with those of material obtained by the pyridine-catalyzed sulfuryl chloride chlorination of 2-*tert*-butylphenol.

Alkylation of 2-ethylphenol with 1-butene. The catalyst was prepared in the autoclave in the usual manner by heating 357.4 g. (2.88 moles) of 2-ethylphenol (prepared as above) with 4 g. (0.15 formula wt.) of aluminum turnings. At a temperature of 215° the reaction mixture was alkylated with 1-butene at 200–500 p.s.i. over a 3-hr. period. Working up the product in the usual manner gave 300 g. (58%) of 2-ethyl-6-*sec*-butylphenol (b.p. 140–141° at 30 mm.; n_D^{20} 1.5153).

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.9; H, 10.2. Found: C, 81.1; H, 9.98.

The phenylurethan of the 2-ethyl-6-*sec*-butylphenol was prepared and found to melt at 132.5–134°.

Anal. Calcd. for $C_{19}H_{23}NO_2$: C, 76.9; H, 7.8. Found: C, 76.5; H, 7.5.

Dealkylation of isobutylene-phenol alkylation products. A sample of phenyl *tert*-butyl ether was refluxed in a system connected to a gas bubbler. Upon boiling at atmospheric pressure for 1 hr. (liquid temperature 182°) only trace amounts of gas were evolved. Similar treatment of 2-*tert*-butylphenol (at 221–222°) and of 4-*tert*-butylphenol (at 237°) gave no evidence of gas evolution.

In order to repeat the above experiments in the presence of aluminum phenoxide, each tube was first charged with 0.01 g. of aluminum turnings and 0.5 g. of phenol. The mixture was briefly heated to effect formation of the phenoxide. To each of the three tubes was then added 5 g. of the desired compound. The tubes were then heated in an oil bath. The ether began to evolve gas at 95° and dealkylated readily at 100°. The 2-*tert*-butylphenol evolved gas rapidly at 190°. The 4-*tert*-butylphenol failed to dealkylate even when refluxed with the catalyst.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ETHYL CORPORATION]

Base-Catalyzed Alkylation with Olefins

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The base catalyzed addition of very weak acids to simple olefins has been studied using the preformed sodium salts of the very weak acids as catalysts. A variety of reactants were employed, and the data are examined in regard to the mechanism of the process.

The base catalyzed addition of very weak acids to activated olefinic systems is a relatively familiar reaction as typified by the addition of alcohols, amines, and acidic hydrocarbons to acrylonitrile,[2a] butadiene,[2b] and styrene.[2c] Although the addition of very weak acids to simple olefins is a somewhat more recent development, four papers[3] and numerous patents[4] have appeared on the subject.

In several of these papers the investigators have relied upon the *in situ* formation of the sodium salt of the very weak acids, which is in reality a reaction intermediate rather than a catalyst in the process.[3b] In the present investigation the sodium salt was preformed before the alkylation step in order to assure somewhat more uniform reaction conditions. The ethylation was applied to a series of compounds including both acidic hydrocarbons and primary and secondary amines. An attempt has been made to correlate the pK_a with the reactivity of the very weak acid.

In general, the greater the pK_a of the very weak acid,[5] the lower the reaction temperature that was required to effect ethylation at a reasonable rate.

Thus cumene (relative pK_a 37)[5] and toluene are readily ethylated at temperatures of 120–140° whereas aniline (relative pK_a 27),[5] methylaniline, and *ortho*-toluidine require temperatures of 240–275°. The aliphatic amines are known to be less acidic than the aromatic amines, as evidenced by their low reactivity with sodamide, and it is found that the temperature required for their ethylation (135–160°) is lower than that required for aniline but higher than that required for toluene.

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[4] Whitman, U. S. Patent **2,448,641** (Sept. 7, 1948) and U. S. Patent **2,501,556** (March 21, 1950); Gresham, Brooks, and Bruner, U. S. Patent **2,501,509** (March 21, 1950); Little, U. S. Patent **2,548,803** (Apr. 10, 1951): Pines and Ipatieff, U. S. Patent **2,670,390** (Feb. 23, 1954) and U. S. Patents **2,721,885–2,721,887** (Oct. 25, 1955); Closson, Kolka, and Ligett, U. S. Patent **2,728,802** (Dec. 27, 1955), U. S. Patents **2,750,384** and **2,750,417** (June 12, 1956), and U. S. Patent **2,751,426** (June 19, 1956).

[5] McEwen, *J Am. Chem. Soc.*, **58**, 1124 (1936).