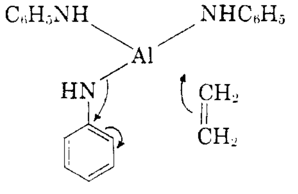
a series of compounds previously available only through multi-step syntheses. The reaction is effected through the use of aluminum anilide type catalysts, and a cyclic mechanism, I, is presumed to be involved, the details of which will be discussed in a forthcoming paper.



I

The following general alkylation procedure was used. The catalyst was prepared by heating the amine with aluminum turnings until hydrogen evolution had ceased. Concentrations of 3.5 to 7 mole-percent of the aluminum anilide were employed. In an experiment using the latter concentration, aniline was alkylated with ethylene at 600–800 p.s.i. and 330° over a seven-hour period in a steel autoclave. The product was hydrolyzed, the aluminum hydroxide removed by filtration, and the material fractionated to yield aniline (0.4%), 2-ethylaniline (1.2%), 2,6-diethylaniline (89%), and some higher-boiling materials. The 2,6-diethylaniline (b.p. 235–236°, n_D^{20} 1.5461; *Anal.* Calc'd for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.9; H, 10.0; N, 9.8) was identified by diazotization to the corresponding phenol, which was found to be identical with an authentic sample of 2,6-diethylphenol on the basis of infrared spectrum and mixture melting point.[1]

The alkylation of aniline with higher olefins proved to be sluggish and a small yield of the branched mono-alkylaniline was the only product from each reaction. Alkylation with propylene gave 2-isopropylaniline (b.p. 217–218°, n_D^{20} 1.5483; hydrochloride, m.p. 182–185°; picrate, m.p. 159–161°),[2] and isobutylene yielded 2-*tert*-butylaniline (b.p. 227–228°, n_D^{20} 1.5450; acetyl derivative, m.p. 161.5–162.5°).[3]

The N-alkylanilines were found to alkylate at considerably lower temperatures than aniline; however, only one alkyl group could be introduced. Thus N-ethylaniline was alkylated with ethylene at 205° to give an 86% yield of N-ethyl-2-ethylaniline (b.p. 223°; n_D^{20} 1.5398. *Anal.* Calc'd for $C_{10}H_{15}N$: N, 9.4. Found: N, 9.6). The product was identified by comparison with an authentic sample produced by the reaction of 2-ethylaniline with ethyl iodide.

The alkylation of N-alkylanilines with higher olefins proceeded readily with olefins of the propylene type ($RCH{=}CH_2$).

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

RESEARCH LABORATORIES
ETHYL CORPORATION
DETROIT 20, MICHIGAN

GEORGE G. ECKE
JOHN P. NAPOLITANO
ALFRED J. KOLKA

Received May 3, 1956

---

[1] All melting points and boiling points are uncorrected.

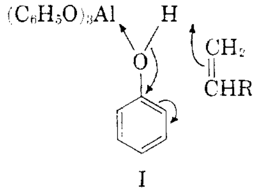
[2] Brown, Bayer, and Blessing, *Ber.*, **57**, 3997 (1924) report the hydrochloride of 2-isopropylaniline to melt at 182° and the picrate to melt at 160°.

[3] Brown and Nelson, *J. Am. Chem. Soc.*, **75**, 24 (1953) report a refractive index of n_D^{20} 1.5453 for 2-*tert*-butylaniline, and Craig, *J. Am. Chem. Soc.*, **57**, 195 (1935) has prepared 2-*tert*-butylacetanilide, m.p. 159–161°.

The *ortho*-Alkylation of Phenols

Sir:

We wish to report a novel alkylation by which 2-alkyl- and 2,6-dialkylphenols may be produced with little or no alkylation occurring at the 4-position. The reaction is that of a phenol with an olefin in the presence of a catalytic amount of the corresponding aluminum phenoxide. The reaction would appear to be analogous to the *ortho*-alkylation of aromatic amines concurrently being reported by these Laboratories; however, it appears that there may be a fundamental difference in the mechanisms. Thus whereas ethylene is more reactive than substituted olefins in the aromatic amine alkylation, the reverse order of reactivity is observed in the phenol alkylation. Details of a cyclic concerted carbonium ion type mechanism, I, will be presented in a forthcoming paper.



I

The reactions were carried out by treating the phenol containing 3–4 mole percent of its aluminum phenoxide with the desired olefin in a steel autoclave. The catalyst was washed from the product with dilute hydrochloric acid and the compounds were isolated by fractional distillation.

Ethylene reacted with phenol at 320° and 600–800 p.s.i. over a ten-hour period to give 24% of 2-ethylphenol (b.p. 201–202°, n_D^{20} 1.5372; 2-ethylphenoxyacetic acid derivative, m.p. 138–140°)[1,2] and 8% of 2,6-diethylphenol (m.p. 37–38°, b.p. 219°).[3]

---

[1] All melting points and boiling points are uncorrected.

[2] Steinkoff and Hopner, *J. prakt. Chem.*, [2], **113**, 140 (1926) report 2-ethylphenoxyacetic acid to melt at 140–141°.

[3] von Auwers and Wittig, *Ber.*, **57**, 1275 (1924) prepared 2,6-diethylphenol, m.p. 37.5–38°.

Phenol was alkylated with propylene at 230–240° and 200–500 p.s.i. over a two-hour period to yield 61% of 2,6-diisopropylphenol (m.p. 19°, b.p. 136° and 30 mm., n_D^{20} 1.5134; *Anal.* Calc'd for $C_{12}H_{20}O$: C, 80.85; H, 10.18. Found: C, 80.8; H, 10.2). The structure was established by chlorination with sulfuryl chloride to yield 2,6-diisopropyl-4-chlorophenol, an authentic sample of which was independently synthesized for comparison. Although small amounts of ethers were present in both the ethylene and propylene alkylation products, no *para*-alkylphenols were isolated.

The alkylation of phenol with isobutylene at 105–115° and 30–100 p.s.i. over a four-hour period gave 5% of recovered phenol, 46% of 2-*tert*-butylphenol (b.p. 120° at 30 mm., n_D^{20} 1.5239),[4] 1% of 4-*tert*-butylphenol, 36% of 2,6-di-*tert*-butylphenol (m.p. 36.5°, b.p. 147° at 30 mm.),[4] and higher-boiling products.

It has been found that the products of the isobutylene alkylation may be varied widely by changes in reaction times, pressures, and temperatures, and products containing from zero to 80% of 2,6-di-*tert*-butylphenol have been obtained. A rudimentary study of the kinetics and thermodynamics of the process has been completed and appears to explain these anomolies.

RESEARCH LABORATORIES
ETHYL CORPORATION
DETROIT 20, MICHIGAN

ALFRED J. KOLKA
JOHN P. NAPOLITANO
GEORGE G. ECKE

---

(4) Pardee and Weinrich, *Ind. Eng. Chem.*, **36**, 596 (1944) have reported 2-*tert*-butylphenol, b.p. 122° at 30 mm. and 2,6-di-*tert*-butylphenol, m.p. 39°.

Received May 3, 1956

Some New Reactions of Nitrogen Iodide with Organic Compounds[1]

Sir:

Although several reactions of nitrogen iodide with organic compounds have been described in the literature,[2,3,4] our preliminary studies with this reagent indicate that some of its most interesting and unusual reactions have thus far escaped attention. For example, although reaction with methyl ketones in aqueous ammonia has been reported to give mainly iodoform,[3] we have been able to isolate as significant products, in the cases of all monofunctional ketones studied, symmetrically substituted pyrazines. Cyclohexanone, 3-pentanone, propiophenone and acetone yield octahydrophenazine (I), 2,5-diethyl-3,6-dimethylpyrazine (II), 2,5-dimethyl-3,6-diphenylpyrazine (III), and 2,5-dimethylpyrazine (IV), respectively. Ethyl acetoacetate, with nitrogen iodide, gives diiodoacetamide (V). Reaction with tyrosine affords 3,5-diiodotyrosine (VI), or a separable mixture of VI and 3-iodotyrosine (VII), depending upon the proportions of reactants employed. Methyl pyruvate yields only iodoform, whereas no reaction is observed with benzene, naphthalene, diethyl ether, ethyl acetate, and acetamide.

Octahydrophenazine (I) was obtained in the following manner. A mixture of 65 g. of iodine and 250 ml. of concentrated aqueous ammonia was stirred mechanically for 10–15 minutes. The supernatant liquid then was decanted from the black solid nitrogen iodide. Next 250 ml. of fresh concentrated aqueous ammonia was added, stirring was resumed, and 27 g. of cyclohexanone was added dropwise over the course of 10–15 minutes with external ice cooling. After the reaction mixture was completely decolorized, stirring was continued for 8 hours and the mixture then was allowed to stand overnight. After addition of 25 g. of sodium bisulfite, the mixture was steam-distilled and the solid thus obtained was filtered from the distillate. Upon vacuum sublimation, 0.72 g. (2.8%[5] based on cyclohexanone) of I, m.p. 106.2–108.0° (uncorr.) was obtained. *Anal.* Calc'd for $C_{12}H_{16}N_2$: C, 76.6; H, 8.6; N, 14.9. Found: C, 76.2; H, 8.6; N, 15.1.

In similar fashion, we obtained II (8–14%) [b.p. 81° (7.6 mm.), n_D^{23} 1.4752, Calc'd for $C_{10}H_{16}N_2$: C, 73.1; H, 9.8; N, 17.1. Found: C, 72.8; H, 10.3; N, 17.0], III (23%) [m.p. 124° (corr.), Calc'd for $C_{18}H_{16}N_2$: C, 83.0; H, 6.2; N, 10.8. Found: C, 82.6; H, 5.9; N, 11.3], and IV [b.p. 58° (21 mm.), isolated as the mercuric chloride adduct or the picrate, in low yield]. Elemental analyses and absorption in the region 3330–3400 cm^{-1} indicate that I, II, and III are contaminated with the corresponding dihydropyrazines.

In the reaction of ethyl acetoacetate with nitrogen iodide, V, m.p. 219–220° (decomp.), (Calc'd for $C_2H_3I_2NO$: C, 7.7; H, 1.0; N, 4.5; I, 81.5. Found: C, 8.0; H, 1.1; N, 4.7; I, 80.8) was obtained in 26% yield, together with an impure solid, m.p. 245–248° (decomp.) which analyzed as a mixture of triiodoacetamide with a small amount of V.

With a 2:1 molar ratio of iodine to tyrosine, we obtained nearly quantitative conversion of tyrosine to VI, m.p. 206° (uncorr.). With a 1:1 ratio, a mixture containing approximately equal amounts of VI and VII, m.p. 204° (uncorr.) was obtained

---

(1) One of us (S.H.W.) is indebted to the University of Kansas for a University Research Grant under which this work was done.

(2) A. A. Petrov, *J. Gen. Chem.* (*U.S.S.R.*), **4**, 1458 (1934); *Chem. Abstr.*, **29**, 3651[5] (1935).

(3) F. D. Chattaway and R. R. Baxter, *J. Chem. Soc.*, **103**, 1986 (1913).

(4) C. Willgerodt, *J. prakt. Chem.*, [II] **37**, 446 (1888).

(5) In these preliminary studies no effort was made to obtain maximum yields.