lowed to shake for the required time period. The sample was then removed, washed with two 50 ml. portions of distilled water, passed through a filter paper to remove traces of water, and analyzed for bisnitrosocyclohexane, nitrocyclohexane, and cyclohexyl nitrate. These operations were repeated at various intervals of time under identical conditions of temperature and pressure until sufficient data were obtained to make the necessary calculations for the desired pressure and temperature. All reactions were carried to at least 70% consumption of the nitroso dimer.

Handling of data. The rate constants were calculated by integration of the first order rate expression using two widely separated time limits[14] and from the slope of the plot of the logarithm of the concentration of bisnitrosocyclohexane *vs.* time. The slope was determined statistically by the method of least mean squares.[15,16] The agreement between the two methods was excellent. The rate constant at 51° was determined by measuring the half-life of bisnitrosocyclohexane under the usual reaction conditions and calculating the rate constant from the half-life.[14]

The activation energy (E_a) was determined from the slope of the curve obtained by plotting the logarithm of the rate constant at various temperatures *vs.* the reciprocal of the absolute temperature[14] and determining the slope of the curve by the method of least mean squares.[15,16] $\Delta H\ddagger$ was determined from the relationship.[6]

$$\Delta H\ddagger = E_A - RT$$

The entropies of activation were calculated from the Eyring equation.[6]

Acknowledgments. The services of Mr. J. L. Swyler and Mr. G. Gesty who carried out the experimental work are deeply appreciated.

The advice and consultation of Dr. G. R. Coraor, Dr. J. D. Roberts, and Dr. C. Gardner Swain were invaluable in carrying out this investigation.

WILMINGTON, DEL.

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[14] Getman and Daniels, *Outlines of Physical Chemistry*, p. 342–386, John Wiley and Sons, Inc., New York, 1947.

[15] Roseveare, *J. Am. Chem. Soc.*, **53**, 1651 (1931).

[16] Reed and Theriault, *J. Phys. Chem.*, **35**, 673 (1931)

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ETHYL CORPORATION]

ortho-Alkylation of Aromatic Amines[1]

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Primary and secondary aromatic amines react with olefins in the presence of aluminum anilide type catalysts to yield products alkylated in the *ortho* positions. No *para* alkylated products were detected.

The nuclear alkylation of aromatic amines by aluminum halide catalyzed reactions has not found wide application because of complications arising from the characteristics of the amino group. It was recently found in these laboratories that primary and secondary aromatic amines could be alkylated with olefins using the corresponding aluminum anilide as the catalyst to give products from which only *ortho*-alkylated amines could be isolated.

TABLE I

REACTIONS OF AROMATIC AMINES WITH OLEFINS USING N-ALUMINO CATALYSTS

Reactants Olefin	Amine	Temperature, °C	Operating Pressure Range, psi	Reaction Time, Hours	Recovered Amine, Mole %	2-Alkyl-Amine Mole %	2,6-Di-Alkylamine Mole %
Ethylene	Aniline	330	450–500	24	29	33	20
Ethylene[a]	Aniline[a]	330	600–800	9	1	2	90[b]
Ethylene	*N*-Methylaniline	205	600–800	3	—	86	—
Ethylene	*N*-Ethylaniline	205	600–800	2.5	2	86	—
Ethylene	*o*-Toluidine	325	600–800	8	—	—	90
Ethylene	α-Naphthylamine	300	600–800	3	55	30	—
Ethylene	*N*-Ethyl-*m*-chloroaniline	255	600–800	3	3	85[c]	—
Propylene	Aniline	330	600–800	5	81	4	—
Propylene	*N*-Methylaniline	235	500–700	4	32	54	—
Isobutylene	Aniline	330	720–730	3	92	2	—
Decene	*N*-Methylaniline	300	90–100	0.5	—	35	—
Cyclohexene	*N*-Methylaniline	300	280–300 (vapor pressure)	0.5	89	2	—

[a] This reaction was carried out using 6.7 mole % of aluminum anilide as compared with 3–4 mole % of catalyst in the other experiments. [b] The dialkylated product consisted of 86% of 2,6-diethylaniline and 4% of 2-ethyl-6-*sec*-butylaniline. [c] Approximately equal amounts of *N*-ethyl-2-ethyl-3-chloroaniline and *N*-ethyl-2-ethyl-5-chloroaniline were produced.

An investigation of the process has made several generalizations possible in regard to the reactivities of the reactants (Table I) and the structures of

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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**, 711 (1956).

[2] Present address, Koppers Co., Inc., Koppers Bldg., Pittsburgh, Pa.

the products (Table II): (1) That only *ortho* alkylated products arise from the reaction; (2) That the reactivities of different types of olefins are $CH_2{=}CH_2 > CH_2{=}CHR > RCH{=}CHR$ or $CH_2{=}CR_2$; (3) That the olefin becomes attached to the aromatic ring at the olefinic carbon atom possessing the larger number of alkyl groups; (4) That *N*-alkylanilines are more reactive than the corresponding primary anilines, although only one alkyl group can be introduced into the ring.

TABLE II

PROPERTIES AND ANALYSES OF ALKYLATION PRODUCTS

Compound	B.P., °C	n_D^{20}	Nitrogen, % Calcd.	Nitrogen, % Found
2-Ethylaniline[a]	209–210	1.5602	11.6	11.4
2,6-Diethylaniline	235–236	1.5461	9.4	9.8
2-Ethyl-6-*sec*-butylaniline	152–153 at 30 mm.	1.5339	7.9	7.9
N-Methyl-2-ethylaniline	216.5	1.5553	10.4	10.9
N-Ethyl-2-ethylaniline	223	1.5398	9.4	9.6
2-Methyl-6-ethylaniline	224	1.5525	10.4	10.6
2-Ethyl-1-naphthylamine[b]	189–190 at 20 mm.	1.6474[c]	8.2	8.2
N-Ethyl-2-ethyl-3-chloroaniline	150.5–151.5 at 30 mm.	1.5556	7.6	8.1[d]
N-Ethyl-2-ethyl-5-chloroaniline	157.5–158.2 at 30 mm.	1.5544		
2-Isopropylaniline[e]	217–218	1.5483	10.3	10.4
2-*tert*-Butylaniline[f]	227–228	1.5450	9.5	9.7
N-Methyl-2-isopropylaniline	224	1.5460	9.4	9.6
N-Methyl-2-(1-Methylnonyl) aniline	138 at 2 mm.	1.5134	5.7	6.0
N-Methyl-2-cyclohexylaniline	112–117 at 2 mm.	1.5644	7.4	7.6

[a] Acetyl derivative m.p. 111–112°, thiourea m.p. 120–120.5°. Braun, Bayer, and Blessing, *Ber.*, **57B**, 392 (1924) report corresponding derivatives of 2-ethylaniline to melt at 113° and 124°. [b] Acetyl derivative m.p. 155–156.5°, Levy, *Ann. chim.*, **9**, 58, (1938) reports the acetyl derivative of 2-ethyl-1-naphthylamine to melt at 156.5°. [c] n_D^{25}. [d] Analysis of mixture of two isomers before refractionation. [e] Phenylthiourea m.p. 134.5–135.5°, hydrochloride m.p. 182–185°, picrate m.p. 159–161° (dec.). Brown, Bayer and Blessing, *Ber.* **57**, 397 (1924) report corresponding derivatives of 2-isopropylaniline to melt at 129–130°, 182°, and 160°. [f] Acetyl derivative m.p. 161.5–162.5°. Craig, *J. Am. Chem. Soc.*, **57**, 195 (1935) reports the acetyl derivative of 2-*tert*-butyl-aniline to melt at 159–161°.

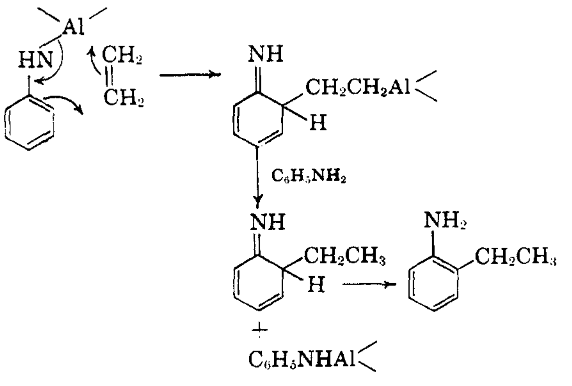
TABLE III

DERIVATIVES OF NEW COMPOUNDS PRODUCED BY ALKYLATION REACTION

Amine	Derivative	M.P., °C	Analysis (% N) Calcd.	Analysis (% N) Found
2,6-Diethylaniline	Acetyl	135–136	7.34	7.26
2-Ethyl-6-*sec*-butylaniline	Benzoyl	198.5–199.5	4.98	4.68
N-Methyl-2-ethylaniline	NO_2BS[a]	133.5–134	8.75	9.07
N-Ethyl-2-ethylaniline	NO_2BS	117.5–118	8.38	8.22
	Benzoyl	47–48	5.53	5.76
2-Methyl-6-ethylaniline	Acetyl	126.5–127.5	8.75	9.07
N-Ethyl-2-ethyl-3-chloro-aniline	Hydrochloride	114–115	6.37	6.21
N-Ethyl-2-ethyl-5-chloro-aniline	Hydrochloride	115–116	6.37	6.19
N-Methyl-2-isopropylaniline	NO_2BS	103–104.5	8.38	8.43

[a] *meta*-Nitrobenzenesulfonyl derivative.

While these observations are inadequate to permit any conclusion to be reached in regard to the mechanism of the reaction, they do provide a basis for the formulation of a hypothesis regarding the nature of the process. Thus, the complete predominance of the *ortho*-alkylated products strongly suggests the geometry imposed by a cyclic intermediate. Since the reactivities of the different types of olefins is that observed in carbanion reactions[3] and is the inverse of that observed in carbonium ion reactions, it would appear that the process, although concerted, is fundamentally a carbanion or free radical type of reaction. An ionic electron shift has been indicated in the equations, although there is no basis for excluding the free radical mechanism at this point. The direction of electron shift, if an ionic process, is indicated by the fact that the olefin becomes attached at the more highly substituted carbon atom.



It might be expected that in both the carbanion

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[3] Pines and Mark, *J. Am. Chem. Soc.*, **78**, 4319 (1956).

and free radical mechanisms the reactivity of the amine would be increased by the presence of an *N*-alkyl group. The failure of the *N*-alkyl amines to react at the second *ortho*-position may result from steric hindrance between the *N*-alkyl and the *ortho*-alkyl group preventing the nitrogen atom from rotating to the angle requisite for the formation of the cyclic intermediate.

Several other mechanisms can be written based on analogy with the aluminum halide catalyzed alkylation of aromatic compounds. These alternatives would be fundamentally carbonium ion type reactions in which the initiation would arise from the interaction of the anilide and the amine:

$$C_6H_5NHR + (C_6H_5NR)_3Al \longrightarrow (C_6H_5NR)_4Al^- + H^+$$

Such a mechanism should exhibit the relative reactivities of different types of olefins typical of acid-catalyzed reactions, which are the inverse of those observed in the *ortho*-alkylation of amines.

The fact that *N*-ethyl-3-chloroaniline required a higher temperature for ethylation than did *N*-ethylaniline suggests partial deactivation of the ring by the electron-withdrawing chlorine atom. It was also of interest that approximately equal amounts of the 2- and the 6-ethyl isomers were produced. This would suggest that the chlorine atom did not cause appreciable steric hindrance.

The presence of 2-ethyl-6-*sec*-butylaniline in the product from the ethylation of aniline was unexpected; however mass spectrometer analysis of a sample of the gas from the autoclave at the conclusion of the ethylation revealed the presence of a small amount of butene (0.8%). Presumably a higher concentration may have been present in the liquid phase, and some alkylation with the butene may have occurred.

EXPERIMENTAL[4]

Preparation of catalysts. The aluminum anilides used as catalysts were prepared by the same general method described in the patent literature.[5] A mixture of 300 ml. of the amine and 4.5 g. (one-sixth formula wt.) of aluminum turnings[6] were stirred and heated under a nitrogen atmosphere until hydrogen evolution became apparent. In the case of aniline, reaction was apparent at 150°. The mixture was stirred and heated until the aluminum had reacted completely. After cooling, the solution was transferred to the autoclave along with an additional 200–300 ml. of the amine. Care was taken throughout the preparation to protect the mixture from moisture and oxygen.

An alternate procedure involved heating the aromatic amine and the aluminum chips in the sealed autoclave until a pressure rise, caused by the evolved hydrogen, became evident. The mixture was then cooled and the hydrogen vented. Somewhat higher temperatures were required to effect catalyst formation by this method, but the resultant catalysts had the same activity as those prepared in glass equipment.

Alkylation procedure. The alkylations were carried out in a two-liter steel autoclave equipped with an anchor-type stirrer (57 r.p.m.) thermocouple well, charging lines, and blow-out disc. After charging the catalyst as described above, the autoclave was flushed with nitrogen and sealed. The stirrer was then started and the mixture heated to 100–150° at which point sufficient olefin was added to give 200–500 p.s.i. of pressure. Heating was then resumed until a temperature was reached where reaction was apparent from a drop in pressure. This temperature was maintained and the autoclave repressured with olefin as required.[7] The reactions were usually continued until the rate of olefin pressure drop became negligible, although in some cases the reaction was stopped before completion. Data on reaction conditions are presented in Table I.

After cooling to room temperature, the pressure was vented and the catalyst hydrolyzed by the addition of water. The aluminum hydroxide was removed by filtration and the water layer separated. The organic layer was again washed and dried by azeotropic distillation with toluene. Fractionation of the product was effected through an appropriate helix-packed column (30–60 theoretical plates). The boiling points, refractive indices and analyses of the products are reported in Table II.

Proof of structure of 2,6-diethylaniline. A 41.1 g. (0.276 mole) portion of the aniline ethylation product boiling at 235–236° was added to a solution of 85 ml. of sulfuric acid in 120 ml. of water. Ice (200 g.) was then added and the mixture maintained at 0–5° by the addition of more ice while 28 g. (0.406 mole) of sodium nitrite dissolved in 60 ml. of water was added. After permitting the mixture to warm to room temperature and remain there for 24 hr., the organic layer was removed. The product was dissolved in 10% sodium hydroxide solution to effect separation from non-phenolic materials and the phenolic compound then liberated by acidification. The product was separated and distilled from a Claisen flask to yield 23.5 g. (57% theory) of 2,6-diethylphenol (b.p. 110–111° at 16 mm.; m.p. 37–37.5°). The melting point of the product was not depressed when mixed with an authentic sample of 2,6-diethylphenol.

Proof of structure of 2-ethyl-6-sec-butylaniline. A 17.7 g. (0.1 mole) quantity of the aniline ethylation product boiling 152–153° (30 mm.) was converted to the corresponding phenol using the diazotization procedure of the above experiment. There was obtained 10 g. (56% theory) of 2-ethyl-6-*sec*-butylphenol (b.p. 85–88° at 2 mm.; n_D^{20} 1.5167), which was identified by comparison with the product of a reaction of 2-ethylphenol and 1-butene.[8] The two samples of the 2-ethyl-6-*sec*-butylphenol had identical infrared spectra and a mixed melting point of the phenylurethanes (m.p. 131.5–133°) showed no depression.

Proof of structure of 2-methyl-6-ethylaniline. A 51.3 g. (0.378 mole) portion of 2-methyl-6-ethylaniline was converted to 2-methyl-6-ethylphenol by the procedure used on the corresponding 2,6-diethyl compound. There was obtained 28 g. (55% theory) of 2-methyl-6-ethylphenol. (b.p. 101–103° at 17 mm.). The phenylurethan of the product was found to melt at 150–151°. (lit. m.p. 150–151°).[9]

Proof of structure of N-ethyl-2-ethylaniline. A mixture of 106 g. (0.87 mole) of 2-ethylaniline and 99 g. (1.0 mole) of potassium carbonate was refluxed with 156 g. (1.0 mole) of ethyl iodide for 1 hr. After washing with 10% potassium

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

[5] D. R. P. 287601. *Chem. Zentr.*, **1915, II,** 992.

[6] The aluminum chips were machined from aluminum metal containing less than one percent of impurities as estimated by spectrographic analysis. The use of aluminum of lower purity was found to necessitate the use of somewhat higher temperatures for catalyst formation.

[7] Ethylene was charged directly from the supply cylinder. Propylene and isobutylene were charged from a specially constructed heated supply tank. Cyclohexene and decene were charged directly to the autoclave along with the amine and the catalyst before heating.

[8] Kolka, Napolitano, Filbey, and Ecke, *J. Org. Chem.*, 22, 642 (1957).

[9] von Auwers, Bundesmann, and Weiners, *Ann.*, **447,** 180 (1926).

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).