acidified with 580 ml. of 3 *N* hydrochloric acid and the *m*-nitrostyrene was removed by steam distillation. A total of 15.5 g. (51%) of *m*-nitrostyrene was obtained, b.p., 85–90° (1 mm.).

Reaction of Enolates with Nitrostyrenes.—The reactions of the active methylene compounds with the nitrostyrenes were all performed in a similar manner. The following example is typical of the whole series.

Reaction of *p*-Nitrostyrene with Ethyl Malonate.—To 100 ml. of absolute ethanol, 0.75 g. (0.033 mole) of clean sodium metal was added. When solution was complete, 25.0 g. (0.15 mole) of ethyl malonate was added, followed by 14.9 g. (0.10 mole) of *p*-nitrostyrene, containing 0.5% hydroquinone. The resulting solution was refluxed for six hours and then allowed to remain overnight at room temperature. The solution was poured into a beaker containing 4 ml. of concentrated hydrochloric acid in 1-l. of water. The product was extracted with ether and the ether extract was washed with water. The extracts were dried over anhydrous sodium sulfate and the solvent removed by distillation. The last traces were removed under vacuum, which caused a small amount of crystalline solid to separate. With the addition of ethanol (50 ml.) and cooling, more of the solid separated. A total of 7.8 g. (34%) of solid (di-addition product) was obtained, m.p., 135–135.5°.

The oil obtained from the above filtrate was distilled. There was obtained 14.1 g. (45%) of a light yellow oil (mono-addition product); b.p. 180–184° (1 mm.).

Reaction of β-(*p*-Nitrophenyl)-ethyl Bromide with Ethyl Malonate.—Ethyl malonate was alkylated with β-(*p*-nitrophenyl)-ethyl bromide using equivalent amounts of reactants and sodium ethoxide in ethanol. A white solid was obtained in 13% yield which was identical with the di addition product obtained from the above reaction of *p*-nitrostyrene with ethyl malonate.

Reaction of *o*-Nitrostyrene with Ethyl β-(*o*-Nitrophenyl)-ethylmalonate.—To 38 ml. of absolute ethanol was added 0.25 g. (0.011 mole) of sodium metal. After reaction was complete, 15.5 g. (0.05 mole) of ethyl β-(*o*-nitrophenyl)-ethylmalonate and 7.5 g. (0.05 mole) of *p*-nitrostyrene were added. The resulting solution was refluxed for 13 hours. The reaction yielded 9.0 g. (39%) of the di-addition product, m.p. 100–101°.

Anal. Calcd. for $C_{23}H_{26}O_8N$: C, 60.25; H, 5.72. Found: C, 59.96; H, 5.86.

Reaction of *p*-Nitrostyrene with Acetylacetone.—To 75 ml. of ethanol was added 0.75 g. (0.033 mole) of sodium. After the reaction was complete 15.0 g. (0.15 mole) of acetylacetone and 14.9 g. (0.10 mole) of *p*-nitrostyrene were added. The resulting solution was refluxed for 12 hours and then allowed to remain overnight at room temperature. The reaction product, isolated as described above, was fractionated under reduced pressure. Five grams of the original *p*-nitrostyrene was recovered together with 7.0 g. (34%) of an orange oil, 5-(*p*-nitrophenyl)-2-pentanone, b.p. 180–184° (1 mm.), n^{20}D 1.5391.

Anal. Calcd. for $C_{11}H_{13}O_3N$: C, 63.75; H, 6.32. Found: C, 63.49; H, 6.31.

The semicarbazone of the above compound was prepared and recrystallized from ethanol, m.p. 175–176°.

Anal. Calcd. for $C_{12}H_{16}O_3N_4$: C, 54.55; H, 6.10. Found: C, 54.31; H, 6.27.

Reaction of *p*-Nitrostyrene with Ethyl Benzoylacetate, Benzoylacetone and Dibenzoylmethane.—To 75 ml. of absolute ethanol was added 0.75 g. (0.033 mole) of sodium. When the reaction was complete 28.8 g. (0.15 mole) of ethyl benzoylacetate and 14.9 g. (0.10 mole) of *p*-nitrostyrene were added and the resulting solution was refluxed for nine hours. The reaction product yielded 8.0 g. of an unidentified oil, b.p. 150–160° (1 mm.), and 5.0 g. (19%) of a white solid, 4-(*p*-nitrophenyl)-1-phenyl-1-butanone, m.p. 109–110°.

Anal. Calcd. for $C_{16}H_{15}O_3N$: C, 71.36; H, 5.61. Found: C, 71.48; H, 5.70.

The semicarbazone of the 4-(*p*-nitrophenyl)-1-phenyl-1-butanone was prepared and recrystallized from ethanol, m.p. 205–205.5°.

Anal. Calcd. for $C_{16}H_{16}O_3N_4$: C, 62.56; H, 5.56. Found: C, 62.44; H, 5.66.

When the above reaction was performed using 24.3 g. (0.15 mole) of benzoylacetone instead of ethyl benzoylacetate, there was obtained 5.5 g. (21%) of 4-(*p*-nitrophenyl)-1-phenyl-1-butanone, 6.0 g. of the original *p*-nitrostyrene and 3.5 g. of an unidentified oil, b.p. 155–160° (1 mm.). However, when dibenzoylmethane (33.6 g., 0.15 mole) was used under the same reaction conditions, 5.6 g. (21%) of 4-(*p*-nitrophenyl)-1-phenyl-1-butanone was isolated together with 6.0 g. of unchanged *p*-nitrostyrene and 13.5 g. (75%) of acetophenone (b.p. 65–70° (1 mm.); semicarbazone, m.p. 197–198°; phenylhydrazone, m.p. 104–105°).

COLUMBIA, MISSOURI

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Disproportionative Condensations. II. The N-Alkylation of Anilines with Primary Alcohols

BY ERNEST F. PRATT AND EVERETT J. FRAZZA[1,2]

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Benzyl alcohol has been found to condense readily with aniline in the presence of potassium benzylate and U.O.P. nickel[2] to give N-benzylaniline. With *para*-substituted benzyl alcohols the reaction rate decreased with decreasing ability of the substituent to release electrons in the order $(CH_3)_2N$, CH_3O, CH_3, H, Cl. The reverse order was obtained when *para*-substituted anilines were condensed with benzyl alcohol. The products were isolated as the pure hydrochlorides in 80 to 90% yields. *p*-Nitroaniline with benzyl alcohol gave *p,p'*-dibenzalaminoazobenzene in 50% yield while cyclohexylamine gave a 49% yield of N-benzalcyclohexylamine. Primary aliphatic alcohols react satisfactorily as exemplified by the 70 to 80% yields of N-*n*-alkylanilines obtained from *n*-hexyl and *n*-decyl alcohols. A reaction course is proposed and evaluated.

Exploratory experiments on the attempted extension of the Guerbet condensation, the subject of the first paper of this series,[3] to the condensation of an alcohol with an amine showed that benzyl alcohol readily condensed with aniline in the presence of potassium benzylate and U.O.P. nickel[2] to give high yields of N-benzylaniline.

$$C_6H_5CH_2OH + C_6H_5NH_2 \longrightarrow C_6H_5CH_2NHC_6H_5 + H_2O \quad (1)$$

In Table I are shown the effects of varying the amount of benzyl alcohol. A xylene solution of the specified amount of benzyl alcohol was treated with 0.04 mole of potassium; 0.125 mole of aniline and 1.0 g. of U.O.P. nickel were then added and the mixture was heated under reflux in an apparatus equipped with a Dean–Stark trap until water evolution was complete. Extraction of an ether solu-

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[1] From the Ph.D. thesis of E. J. Frazza, Feb., 1954.

[2] National Institutes of Health Fellow, 1952–1954.

[3] E. F. Pratt and D. G. Kubler. THIS JOURNAL, **76**, 52 (1954).

tion of the products with aqueous hydrochloric acid gave N-benzylaniline hydrochloride as the pure solid.

TABLE I

EFFECT OF VARYING THE AMOUNT OF BENZYL ALCOHOL ON THE N-BENZYLATION OF ANILINE

Alcohol, mole	Water, %	Product, %
0.125	47	49
.156	66	67
.187	87	92
.250	99	89

The decrease in yield of product and of water as the amount of benzyl alcohol was decreased (Table I) was in part due to the fact that since 0.04 mole of the alcohol was converted to potassium benzylate less than the stoichiometric amount of alcohol was present in the first two experiments. A second contributing factor was the precipitation of potassium benzylate as conversion of benzyl alcohol to N-benzylaniline proceeded; this precipitation was, of course, most serious when least benzyl alcohol was used. Under the conditions of the last experiment of Table I, however, little if any precipitate appeared until the reaction was 60% complete and at no time was more than a small amount of precipitate present. This experiment, which is identical with the third and fifth experiment of Tables II and III, respectively, as well as with the second and seventh experiment of Table IV, will hereafter be called the reference experiment. For the experiments of Table I the "rate curves," obtained by plotting the percentage of water collected *vs.* time were roughly superimposable until the yield of water was within 5% of its final value.

TABLE II

EFFECT OF VARYING THE AMOUNT OF POTASSIUM ON THE N-BENZYLATION OF ANILINE

K, mole	$t^{a}_{25\%}$, min.	Water, %	Product, %
0.005	715	94	..[b]
.02	316	101	86
.04	213	99	89
.06	144	93	92
.08	60	87	88
.10	32	67	69

[a] This is the time in which a 25% yield of water collected.
[b] Product not isolated.

One-fourth mole of alcohol was used in the study of the effect of varying the amount of potassium (Table II). Excellent yields of product and water were obtained when less than 0.06 mole of potassium was used. With larger amounts of potassium the yields decreased, apparently because the potassium benzylate precipitated to a more serious extent, possibly occluding significant amounts of the reactants. The time required for a 25% yield of water to collect decreased consistently with increasing amounts of potassium. Data for the "rate curves" are given in the Experimental. With 0.005 mole of potassium the rate of water evolution gradually increased and then gradually decreased while with larger amounts of potassium there was a consistent change until with 0.10 mole of potassium the rate decreased throughout. The foregoing statement disregards the 3 to 7% of water which was usually evolved almost instantaneously even in the absence of aniline.

In the study of the effect of varying the amount of U.O.P. nickel 0.04 mole of potassium and 0.250 mole of benzyl alcohol were used (Table III).

TABLE III

EFFECT OF VARYING THE AMOUNT OF U.O.P. NICKEL ON THE N-BENZYLATION OF ANILINE

U.O.P. nickel, g.	Time,[a] min.	Water, %	Product, %	Hydrogen, mole
0.0313	1980	105[b]	96	0.001
.125	1075	109[b]	93	.002
.25	615	100	94	.015
.50	524	99	90	.017
1.00	424	99	89	.031

[a] This is the time in which a 90% yield of water collected.
[b] The source of the excess water is unknown.

The "rate curves" were all of the elongated S shape of the reference experiment and the yields averaged 92%. When a large amount of nickel (8.0 g.) was used the yield dropped to 61% and a significant amount of benzaldehyde was isolated; part of the aniline may have been lost *via* undetermined side reactions. It was of considerable interest to find that a 94% yield of N-benzylaniline could be obtained easily at higher temperatures in the absence of nickel. This was accomplished by refluxing a mixture of the alcohol, amine and potassium benzylate in the standard apparatus for 50 minutes during which the temperature rose from 189 to 227°.

It is apparent from the data in Table IV that a variety of *para*-substituted N-benzylanilines may be prepared in 80 to 90% yields. Except for the indicated changes in reactants the procedure of the reference experiment was used. The "rate curves" were of the same elongated S shape and were found to be satisfactorily reproducible. A consistent increase in rate with increasing ability of the *para* substituent of the benzyl alcohol to release electrons was observed while the same changes in the *para* substituent of the aniline had the opposite effect.[4]

TABLE IV

EFFECT OF CHANGING THE *para* SUBSTITUENTS

para Substit.	Time,[a] min.	Water,[b] %	Product, %
para-Substituted benzyl alcohols and aniline			
Cl	1183	102	78
H	424	99	89
CH_3	396	107	89
CH_3O	312	107	84
$(CH_3)_2N$	222	99	85
para-Substituted anilines and benzyl alcohol			
Cl	281	104	87
H	424	99	89
CH_3	524	108	93
CH_3O	603	110	88
$(CH_3)_2N$	727	115	93

[a] This is the time in which a 90% yield of water collected.
[b] The source of the excess water produced in certain cases is unknown.

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[4] Revised values for the relative electron releasing abilities of these substituents are given by H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

p-Chlorobenzyl alcohol, however, reacted much more slowly than would have been predicted on the basis of the rates for the other benzyl alcohols. *p,p'*-Dichlorobenzylaniline, *p*-chloro-*p'*-methoxybenzylaniline and *p*-methoxy-*p'*-chlorobenzylaniline were prepared under the same conditions. About 80% yields were obtained and the rates agreed qualitatively with those expected from the results of Table IV.

When the reaction of *p*-nitroaniline and benzyl alcohol was attempted *p,p'*-dibenzalaminoazobenzene precipitated from the reaction mixture in 50% yield. It is probable that *p,p'*-diaminoazobenzene and benzaldehyde were produced by a previously reported reaction[5] and these products reacted with each other to give the compound isolated. This last step was carried out independently to give comparison material which proved to be identical.

Only a 5% yield of water was obtained from the attempted reaction of *n*-hexyl alcohol and *n*-hexylamine, while this amine and benzyl alcohol gave a mixture of unidentified products. The α-branched cyclohexyl- and 1,1,3,3-tetramethylbutylamine with benzyl alcohol gave the Schiff bases (reaction 3) in about 50% yields.

The primary aliphatic alcohols, *n*-hexyl and *n*-decyl were converted to the desired N-*n*-alkylanilines in 70 to 80% yields. Cyclohexanol gave a 19% yield of N-cyclohexylaniline and significant amounts of the corresponding anil. Ill-defined products, a large proportion of which were undistillable, were obtained from octanol-2 as well as α-methylbenzyl alcohol with aniline.

The following course of reaction is proposed.

$$C_6H_5CH_2OH \xrightarrow{Ni} C_6H_5CHO + H_2 \tag{2}$$

$$C_6H_5CHO + C_6H_5NH_2 \longrightarrow C_6H_5CH{=}NC_6H_5 + H_2O \tag{3}$$

$$C_6H_5CH{=}NC_6H_5 + C_6H_5CH_2OH \xrightarrow{C_6H_5CH_2OK} C_6H_5CH_2NHC_6H_5 + C_6H_5CHO \tag{4}$$

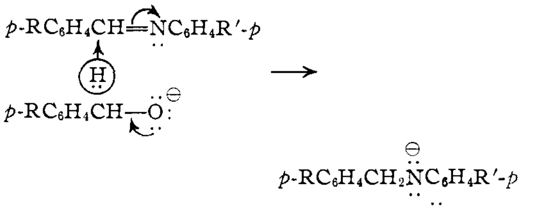
Since U.O.P. nickel was found to catalyze the over-all reaction and the amount of hydrogen evolved was found to increase consistently as the amount of nickel was increased (Table III) the occurrence of reaction 2 is indicated. Then, too, benzaldehyde was isolated when a large amount of nickel was used and benzoic acid was always formed in small amounts, most probably *via* a Cannizzaro reaction of the aldehyde. The low yields of hydrogen suggest, however, that reaction 2 is needed only to initiate the process and that most of the aldehyde reacting in 3 is furnished by reaction 4; the over-all reaction 1 is the sum of 3 and 4 only. Since, as noted above, nickel is not required at the higher temperatures at least a trace of aldehyde to initiate reaction 3 apparently results from thermolytic dehydrogenation or some other types of oxidation of the benzyl alcohol.

Reaction 3 is known to proceed with such outstanding ease that there is little question that it will occur so long as aldehyde is provided *via* reactions 2 or 4. The Schiff bases were isolated in certain cases and a high yield of water was always collected.

Excellent evidence for the occurrence of reaction 4, as well as 3, was obtained in a series of three experiments in which anil was added and the nickel omitted. The procedure of the reference experiment was used with 2.5, 10 and 40% of the aniline and an equivalent amount of the benzyl alcohol replaced by corresponding amounts of benzalaniline. The reaction proceeded readily in each case, the rate increasing in direct proportion to the amount of benzalaniline added. With 10% added anil the "rate curve" was almost exactly superimposable on the 10 to 100% portion of the "rate curve" for the reference experiment. In each case benzalaniline was isolated in over 93% yield and water was collected in over 97% yield calculated on the basis of reactions 3 and 4. Reactions like 4 were doubtless accomplished by Diels and Rhodius[6] although they did not isolate the aldehyde.

Benzalaniline was shown to be present in significant amounts during the middle stages of the reaction in two experiments like the reference experiment except that the reaction was quenched when a 25% and when a 75% yield of water had collected. Only 3 and 10% yields of benzalaniline were obtained, but considerably more than this may well have been present since the required separations were difficult and since the N-benzylaniline hydrochloride was isolated in only 3 and 37% yields.

Since the nickel catalyzed reaction 2 appears to play a relatively minor role, except during the early stages, the potassium benzylate catalyzed[6] reaction 4 becomes the most probable chief rate controlling reaction during the latter two-thirds of the process. The increasing rates found with increasing amounts of added anil and the isolation of anil when the reaction was stopped prematurely are consistent with this interpretation. Furthermore, the effects on the rate of changing the *para* substituents of both the amine and the alcohol (Table IV) are opposite to those found for reaction 3[7]; these effects are interpretable, however, on the basis that reaction 4 chiefly controls the rate and that its mechanism is analogous to that proposed for the Meerwein–Ponndorf–Verley reduction.[8]



(5)

Thus when R is changed from hydrogen to the strongly electron-releasing methoxyl the shift of electrons from the anil double bond toward the nitrogen would prevent any large increase in electron density at the carbon and its ability to accept a hydrogen with its electrons from the benzylate ion would not be diminished greatly. No such shift of electrons away from the carbon singly bonded to the oxygen of the benzylate ion is possible, however,

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[5] F. B. Dains and W. O. Kenyon, THIS JOURNAL, **53**, 2357 (1931), and references therein.

[6] O. Diels and R. Rhodius, *Ber.*, **42**, 1072 (1909).

[7] To be published with M. J. Kamlet.

[8] W. von E. Doering and T. C. Ashner, THIS JOURNAL, **75**, 393 (1953).

so that a *p*-methoxyl group in the benzylate ion would tend to facilitate the shift of the hydrogen with its electrons and increase the rate as was found experimentally. When R′ is changed from hydrogen to methoxyl, the electrons of the anil double bond would tend to be displaced toward the carbon which would hinder the shift of the hydrogen with its electrons and the rate would tend to decrease which again agrees with the experimental results.

The very gradually increasing rates as measured by water evolution encountered during the early stages in all experiments of Tables I, III and IV were much like those found with the Guerbet condensation.[3] In both cases this induction period may well have been a measure of the time needed for sufficient aldehyde to be formed *via* reaction 2. Since the reaction course suggested here is closely related to that proposed for the Guerbet condensation the evidence for one reaction sequence lends support to the other.

Many well-known examples of the alkylation of amines by alcohols are to be found in the literature. These have usually been carried out in an autoclave in the neighborhood of 200° with an acidic or a hydrogenation–dehydrogenation catalyst.[9] Since a basic catalyst has not ordinarily been used and since tertiary amines usually have been a major or minor product it was in many cases impossible and in the remaining cases it seems improbable that reaction proceeded primarily *via* the disproportionation process of reaction 4. An apparent exception, however, is the attempted reduction of the aromatic ring of 2-aminophenylacetic acid with sodium and 2-methylbutanol-1 in which an unspecified amount of N-alkylation occurred.[10]

Experimental[11]

General Procedure.—All starting materials were purified by standard methods until their refractive indices or melting points agreed closely with the literature values. The *p*-chlorobenzyl alcohol was prepared in 70% yield by Mr. D. A. Lima by reduction of the aldehyde with sodium borohydride according to the published method for the reduction of anisaldehyde.[12]

The standard procedure will be described for the reference experiment which is the fourth, third and fifth experiment of Tables I, II and III, respectively, as well as the second and seventh experiment of Table IV. Except for obvious modifications this procedure was used in all cases unless otherwise noted. One-fourth mole of benzyl alcohol was dissolved in sufficient xylene to give 50 ml. of solution and placed in a 500-ml. three-necked flask. One neck of the flask held an asbestos wrapped Dean–Stark trap filled with xylene and surmounted by a condenser while the other two necks held a gas inlet tube and a thermometer. Stirring by means of a magnetic stirrer was begun and the system was swept with nitrogen for at least 5 minutes. Slow introduction of nitrogen was continued while 0.04 mole of clean potassium was added with cooling at such a rate that the temperature did not exceed 70°. When the potassium had reacted completely the stirrer and the nitrogen stream were stopped and 0.125 mole of aniline dissolved in sufficient xylene to give 50 ml. of solution was added together with 1.0 g. of U.O.P. nickel, 25 ml. of xylene and boiling chips. The U.O.P. nickel, obtained as pellets,[2] was crushed to pass a 100-mesh sieve. The mixture was heated with a hemispherical mantle so that it boiled vigorously. The gas which escaped from the top of the condenser after refluxing began was collected over water in an inverted 4-l. graduated cylinder. At suitable intervals the temperature and the volumes of water and of gas were recorded. Refluxing was continued for at least 2 hr. after water evolution stopped.

One hundred ml. of water and 100 ml. of ether were added to the cooled reaction mixture and the catalyst was filtered off and washed with 20 ml. of ether. The ether layer was separated and washed with 10 ml. of 10% aqueous sodium hydroxide and then with water until neutral to litmus. After washing the combined aqueous layers with two 50-ml. portions of ether they were concentrated by evaporation. The small amount of benzoic acid which precipitated upon acidification with hydrochloric acid was filtered off and dried. Upon shaking the combined ether layers with 80 ml. of 10% aqueous hydrochloric acid the N-benzylaniline hydrochloride precipitated and was filtered off. The crystals were washed three times by stirring with 100-ml. portions of ether and filtering. Unless otherwise noted the yields tabulated are for the hydrochlorides. Except for the one case noted below the melting points or refractive indices of all known products agreed satisfactorily with the literature values.

In several representative cases the collected gas was analyzed by comparing its rate of effusion through an orifice with that of pure hydrogen.[13] Qualitative tests showed the absence of carbon monoxide and carbon dioxide. On the assumption that the impurity was air the dry gas was found in every case to contain over 90% hydrogen.

Experiments of Tables I, II and III.—The modifications of the standard procedure required for the experiments of these tables are obvious. In the experiments of Table I the temperature, for the 10 to 90% portion of the reaction, increased consistently from 142.3 ± 0.7° to 144.2 ± 0.7° as the amount of alcohol was increased. The amount of hydrogen varied from 0.02 to 0.03 mole and the amount of benzoic acid from 0.007 to 0.019 mole, but in neither case were any consistent trends observed.

The N-benzylaniline hydrochloride isolated in the typical case melted at 214–215° (lit. m.p. 215–216°). Upon shaking the hydrochloride with excess aqueous sodium hydroxide, extracting with ether, drying the extract over solid sodium hydroxide and concentrating by evaporation a 95% yield of the free amine which melted at 36–37° was obtained (lit. m.p. 37–38°). Treatment with benzoyl chloride gave N-phenyl-N-benzylbenzamide which melted at 106–107° (lit. m.p. 107°).

The shape of the "rate curves" changed markedly as the amount of potassium was varied in the experiments of Table II. The number of minutes required for the production of a 10, 15, 20, 30, 40, 50, 60, 70, 80 and 90% yield of water were: (0.005 mole of potassium) 463, 563, 641, 775, 896, 1020, 1132, 1248, 1347 and 1465; (0.02 mole of potassium) 180, 222, 268, 354, 432, 503, 578, 638, 705 and 752; (0.04 mole of potassium) 25, 113, 169, 240, 291, 335, 365, 386, 407 and 424; (0.06 mole of potassium) 6, 25, 103, 168, 205, 226, 242, 257, 280 and 355; (0.08 mole of potassium) 7, 15, 30, 90, 114, 138, 166, 213 and 309 (water evolution stopped at 87%); (0.10 mole of potassium) 6, 10, 18, 53, 93, 150 and 253 (water evolution stopped at 67%). Somewhat surprisingly, the temperature decreased consistently from 146.0 ± 0.6° to 141.7 ± 0.7° as the amount of potassium was increased. The amount of hydrogen increased from 0.03 to 0.06 mole and the amount of benzoic acid from 0.007 to 0.027 mole.

As might have been expected there were no significant changes in temperature as the amount of nickel was varied in the experiments of Table III; among all the experiments the temperature was 144.2 ± 1.0° while within a single experiment the variation was only about half as large. The

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(9) The most pertinent references are: E. Knoevenagel, *J. prakt. Chem.*, **89**, 1 (1914); A. J. Hill and J. J. Donleavy, *Ind. Eng. Chem.*, **13**, 504 (1921); A. Mailhe and F. de Godon, *Compt. rend.*, **172**, 1417 (1921); A. B. Brown and E. E. Reid, THIS JOURNAL, **46**, 1836 (1924); K. Rosenmund and A. Joithe, *Ber.*, **58B**, 2054 (1925); A. Guyot and N. Fournier, *Bull. soc. chim.*, **47**, 203 (1930); S. A. Busse and A. I. Travin, *J. Russ. Phys. Chem. Soc.*, **62**, 1685 (1930); E. J. Schwoegler and H. Adkins, THIS JOURNAL, **61**, 3499 (1939), and references therein; R. Mozingo, C. Spencer and K. Folkers, *ibid.*, **66**, 1859 (1944).

(10) E. Einhorn and H. Pfeiffer, *Ann.*, **320**, 218 (1899).

(11) All melting points are corrected. We are indebted to Professor Mary Aldridge and Miss Katherine Gerdeman for the analyses.

(12) S. W. Chaikin and Weldon G. Brown, THIS JOURNAL, **71**, 122 (1949).

(13) R. B. Ellis and A. P. Mills, "Laboratory Manual in Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1953, p. 11.

amount of benzoic acid increased from 0.003 to 0.009 mole as the amount of nickel was increased.

Reaction of *para*-Substituted Benzyl Alcohols and Aniline.—In the experiments of Table IV there was no consistent variation in the temperature or in the amount of hydrogen or acid. For practically all of the experiments the temperature was 145.0 ± 1.3°; the amount of hydrogen varied from 0.015 to 0.045 mole and the amount of acid from 0.005 to 0.025 mole.

Because of the basicity of *p*-dimethylaminobenzyl alcohol the procedure for isolating the product from this alcohol (Table IV) was modified. The ether layer remaining after the standard alkali and water extractions was washed with saturated aqueous sodium chloride and dried over "Drierite." Upon recrystallization from aqueous ethanol of the residue obtained upon removal of the solvents a first crop of 9.1 g. (m.p. 71.5–72.5°, lit. m.p. 72–73°) and a second crop of 3.0 g. (m.p. 68–69.5°) of **N-(*p*-dimethylaminobenzyl)-aniline** was obtained.

The **N-benzyl-*p*-chloroaniline hydrochloride** appears to be new. Recrystallization from alcohol–ether gave colorless plates which melted at 195–196°. *Anal.* Calcd. for $C_{13}H_{13}NCl$: C, 61.43; H, 5.15; N, 5.51. Found: C, 61.35; H, 4.98; N, 5.85.

A 93% yield (29.1 g.) of **N-benzyl-*p*-methoxyaniline hydrochloride** (Table IV) was obtained in the standard fashion as colorless needles which melted at 183–184.5°. Since the hydrochloride is new the known free base was regenerated as described in the following paragraph. An 88% yield (23.5 g.) of N-benzyl-*p*-methoxyaniline was obtained as yellow plates which melted at 50–51° (lit. m.p. 50–51°).

In the attempted isolation of **N-benzyl-*p*-dimethylaminoaniline hydrochloride** (Table IV) no precipitate formed when the organic layer was treated with 10% aqueous hydrochloric acid in the standard fashion. The aqueous layer was, therefore, washed with ether and made alkaline with sodium hydroxide. The oil which separated was removed by multiple ether extraction, the extracts were combined, washed with water until neutral, treated with carbon and dried over potassium hydroxide. Upon concentration of the ether solution 26.4 g. of the N-benzyl-*p*-dimethylaminoaniline was obtained as light yellow crystals which melted at 45–46°.

When **N-(*p*-methoxybenzyl)-*p*-chloroaniline hydrochloride** was prepared under the standard conditions the time for a 90% yield of water to collect, the yields of product and water and the melting point were: 267 min., 85%, 111% and 178–179°, respectively. *Anal.* Calcd. for $C_{14}H_{15}Cl_2NO$: C, 59.17; H, 5.32; N, 4.93. Found: C, 59.50; H, 5.10; N, 5.18. For **N-(*p*-chlorobenzyl)-*p*-methoxyaniline hydrochloride** the data in the same sequence were: 3,545 min., 78%, 91% and 205–206°. Found: C, 59.46; H, 5.24; N, 5.20. For **N-(*p*-chlorobenzyl)-*p*-chloroaniline hydrochloride** the results were: 928 min., 79%, 102% and 198–199°. *Anal.* Calcd. for $C_{13}H_{12}Cl_3N$: C, 59.17; H, 5.32. Found: C, 59.50; H, 5.18.

The reaction of *p*-nitroaniline and benzyl alcohol in the standard fashion gave an orange precipitate. In 13 minutes 0.25 mole of water was evolved and after two days water evolution stopped at 0.38 mole. The slurry obtained upon adding 100 ml. of water and 100 ml. of ether to the reaction mixture was filtered. Upon dissolving the product in methanol, removing the catalyst by filtration and concentrating the filtrate 12.2 g. of ***p,p'*-dibenzalaminoazobenzene** was obtained. Two recrystallizations from ethyl acetate raised the m.p. from 203–204° to 206–207°. *Anal.* Calcd. for $C_{26}H_{20}N_4$: C, 80.50; H, 5.18; N, 14.42. Found: C, 80.48; H, 5.07; N, 14.95.

Authentic material for a mixture m.p. determination was prepared by Mr. D. A. Lima. A benzene solution containing 0.08 mole of *p,p'*-diaminoazobenzene, 0.16 mole of benzaldehyde and a trace of *p*-toluenesulfonic acid was refluxed in an apparatus fitted with a Dean–Stark trap until water evolution was complete (90% yield). After the catalyst was extracted with water and the benzene solution concentrated the resultant precipitate was filtered off and recrystallized from ethyl acetate. A 63% yield of orange plates which melted at 205–206° was obtained. A melting point determination on a mixture of the material from the two sources showed no depression.

Reactions of Other Alcohols with Aniline.—The reaction of cyclohexyl alcohol and aniline under the standard conditions gave a 111% yield of water in 5 days. By distillation of the combined ether layers, obtained in the standard fashion, 13.0 g. of a viscous liquid was collected at 135–138° (12 mm.). Upon shaking a solution of this in petroleum ether with aqueous hydrochloric acid a 19% yield (4.9 g.) of **N-cyclohexylaniline hydrochloride** was obtained (m.p. 201–202°, lit m.p. 202–203°). One recrystallization from alcohol–ether gave a 12% yield of white needles which melted at 206–207°. Because of the high m.p. it was analyzed. *Anal.* Calcd. for $C_{12}H_{18}ClN$: C, 68.07; H, 8.57; N, 6.62. Found: C, 68.37; H, 8.42; N, 6.86. The petroleum ether layer was separated and washed with water. Upon removal of the solvent and treatment of the residue with 2,4-dinitrophenylhydrazine 1.7 g. of the hydrazone of cyclohexanone was obtained (m.p. 158–159°, lit. m.p. 162°).

n-Decyl alcohol reacted under the standard conditions to give a 111% yield of water in 22 hours. Distillation through an 8-inch Vigreux column as in the preceding paragraph gave 0.06 mole of *n*-decyl alcohol and then 26.3 g. of N-*n*-decylaniline at 109–113° (0.1 mm.). Upon redistillation 22.1 g. (76%) was obtained at 116–119° (0.15 mm.), $n^{25}D$ 1.5058. *Anal.* Calcd. for $C_{16}H_{27}N$: C, 82.33; H, 11.66; N, 6.00. Found: C, 82.66; H, 11.55; N, 5.71.

N-*n*-Decylaniline hydrochloride was obtained by treating a petroleum ether solution of the amine with gaseous hydrogen chloride. Recrystallization twice from the same solvent gave colorless needles which melted at 90–91° and which were soluble in ether and in absolute ethyl alcohol. *Anal.* Calcd. for $C_{16}H_{28}ClN$: C, 71.21; H, 10.46; N, 5.19. Found: C, 71.61; H, 10.18; N, 5.49.

With *n*-hexyl in place of *n*-decyl alcohol the results were similar except that the 22.1 g. of material which distilled at 143–154° (16 mm.), $n^{25}D$ 1.5191, appeared to be a mixture of 2-butyloctanol-1, the product of a Guerbet reaction (lit. b.p. 132° at 15 min., $n^{25}D$ 1.440) and **N-*n*-hexylaniline** (see following paragraph for physical constants on material which analyzed satisfactorily). Due primarily to the solubility of N-*n*-hexylaniline hydrochloride in organic solvents a satisfactory separation was not achieved. It was calculated, from the refractive indices, that the yield of desired product was 83%. The corresponding products were more readily separable by distillation in the preceding case.

In a similar experiment using twice as much aniline (*i.e.*, 0.250 mole of *n*-hexyl alcohol, 0.250 mole of aniline and 0.04 mole of potassium) to minimize the Guerbet side reaction, water evolution stopped at 66% (2.96 ml.) after 16 hours. Stirring was initiated to alleviate the bumping which began when much precipitate formed midway in the reaction. Distillation through the 8-inch Vigreux column afforded 26.3 g. (59%) of N-*n*-hexylaniline which boiled at 141–144° (13 mm.), $n^{25}D$ 1.5204. This material had been prepared previously but since only its b.p. was given[14] it was analyzed. *Anal.* Calcd. for $C_{12}H_{19}N$: C, 81.30; H, 10.80; N, 7.90. Found: C, 81.25; H, 10.66; N, 8.24. The *p*-toluenesulfonamide derivative was prepared and found to melt at 66.5–67.0° (lit. m.p. 67–68°). If it is assumed that the 0.04 mole of potassium prevented the reaction of an equivalent amount of alcohol the yield rises to 70%.

Reaction of Other Amines with Benzyl Alcohol.—When cyclohexylamine and benzyl alcohol reacted under the standard conditions water evolution stopped at 89% (0.118 mole). It is noteworthy that an approximately equivalent amount of hydrogen (0.123 mole) was collected; this together with the fact that the Schiff base rather than the product amine was isolated suggests that reactions 2 and 3 predominated here. By distillation 11.3 g. (49%) of **N-benzalcyclohexylamine** was obtained at 83–85° (0.08 mm.), $n^{25}D$ was 1.5500, as compared to the literature value of 1.5502.[15] A small amount of the product was hydrolyzed and the 2,4-dinitrophenylhydrazone of benzaldehyde prepared as described in the following paragraph; this derivative melted at 237–238°.

The reaction of 1,1,3,3-tetramethylbutylamine with benzyl alcohol under the standard conditions gave a 48% yield of water in 3 days. This amine was chosen since, in contrast to other primary amines, it is reported to form very stable Schiff bases with aldehydes.[16] By distillation 12.3 g. (47%) of **N-benzal-1,1,3,3-tetramethylbutylamine** was ob-

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[14] W. J. Hickinbottom, *J. Chem. Soc.*, **1119** (1937).

[15] T. J. West, *J. Soc. Chem. Ind.*, **61**, 158 (1942).

[16] Technical Bulletin SP-33 12/52, Rohm and Haas Co., Washington Square, Philadelphia 5, Pa. We wish to thank Rohm and Haas for a generous sample of the amine.

tained at 134–135° (10 mm.), n^{25}_{D} 1.5136. *Anal.* Calcd. for $C_{15}H_{23}N$: C, 82.89; H, 10.67; N, 6.45. Found: C, 83.15; H, 10.46; N, 6.40. Since this compound appeared to be stable to acid at room temperature it was hydrolyzed by boiling with 10% aqueous hydrochloric acid for one hour. The benzaldehyde was extracted into ether, the ether evaporated, and the residual oil converted to the 2,4-dinitrophenylhydrazone. After recrystallization from aqueous ethanol a 65% yield of orange plates which melted at 235–236° was obtained (lit. m.p. 238–239°).

Supplementary Experiments.—In the experiment using 8.0 g. of U. O. P. nickel the standard conditions were used except that a magnetic stirrer was employed throughout to prevent violent bumping. A 114% yield of water was collected in about 8 hours. In the usual fashion 16.7 g. of N-benzylaniline hydrochloride and 1.2 g. of benzoic acid were isolated. The ether layer remaining after the usual acid extraction had a strong benzaldehyde odor and gave a precipitate with 2,4-dinitrophenylhydrazine. Upon shaking the ether layer for one hour with 100 ml. of saturated sodium bisulfite solution a solid precipitated. After filtering, washing and drying this bisulfite addition product of benzaldehyde weighed 12.7 g.

In the experiment to test whether nickel was needed at high temperatures 0.750 mole of benzyl alcohol, 0.375 mole of aniline and 0.12 mole of potassium were used with no solvent. After refluxing for 50 minutes at 189 to 227° the reaction was stopped; the volume of the aqueous layer was 5.9 ml. In order to facilitate separation of the layers in the Dean–Stark trap the lower part of the trap was immersed in a water-bath held at about 90°. In the usual fashion 77.1 g. of N-benzylaniline hydrochloride was isolated. It seems probable that at these higher temperatures less potassium and a smaller excess of alcohol could be used without lowering the yield.

In the series of three experiments using added benzalaniline equivalent to 2.5, 10 and 40% of the amount of aniline the amounts of benzyl alcohol and aniline were decreased correspondingly. Thus for example when 0.0125 mole (10%) of benzalaniline was employed 0.2375 mole of benzyl alcohol and 0.1325 mole of aniline were used. No nickel was employed and the standard procedure was followed in other respects. The yields of N-benzylaniline hydrochloride were 94, 95 and 93% while the yields of water were 111, 90 and 98%, respectively. The times required for a "50% yield of water" to collect, determined by adding the percentage of benzalaniline used to the percentage of water collected were 792, 203 and 8 minutes while the times required for a "90% yield of water" were 1201, 306 and 43 minutes, respectively.

In the two experiments that were quenched when a 25 and a 75% yield of water had collected the standard conditions were used, but the scale was quadrupled in order to facilitate the required separations. The reactions were quenched at the desired point by cooling rapidly and by adding water and ether. After the benzoic acid was obtained from the aqueous layers in standard fashion the combined organic layers were dried and the ether, xylene, aniline and benzyl alcohol removed by distillation up to a final temperature of 115° at 15 mm. N-Benzylaniline was removed from the residue by thoroughly shaking an ether solution with 10% aqueous hydrochloric acid and filtering. The filtrate containing benzaldehyde from the hydrolysis of the anil was washed with water until neutral and stirred 2 hours with 400 ml. of a saturated aqueous solution of sodium bisulfite. The washed and dried precipitate of the sodium bisulfite addition product of benzaldehyde amounted to 0.017 mole for the experiment stopped at a 25% yield of water and the precipitate amounted to 0.049 mole for the experiment stopped when a 75% yield of water had collected.

In an experiment exactly like the reference experiment except that sodium was used in place of potassium a 75% yield of water collected in 526 minutes (the corresponding time with potassium was 395 minutes) and water evolution stopped at 92% after a large amount of alkoxide suddenly precipitated. A 57% yield of N-benzylaniline hydrochloride was isolated in the standard fashion. If the extensive precipitation of alkoxide could be avoided, possibly by using less sodium along with higher temperatures to speed up the reaction, it appears probable that the yield could be raised. The slow conversion of sodium to the alkoxide is, however, another point against its use.

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[CONTRIBUTION FROM THE MARION EDWARDS PARK LABORATORY OF BRYN MAWR COLLEGE]

Relative Rates of Iodination of *p*-Alkylanilines

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The rates of iodination of *p*-alkylanilines in aqueous methanol indicate the predominant operation of the inductive effect by the alkyl groups at the *meta* positions. The order of electron release by alkyl groups is discussed in terms of the nature of the substituting agent.

In a previous communication it was shown that *p*-alkylphenols are iodinated *meta* to the alkyl groups in an order which indicates the predominant operation by the alkyl groups of the general inductive effect.[2] We now report the similar iodination of *p*-alkylanilines, which is free from the complication which might be caused by the ionization of the phenols, because the anilinium ion forms appreciably only at low *p*H, and, unlike free phenol, it cannot be considered a serious participant in aromatic halogenation at moderately high *p*H. The substitution of the free amines should therefore give a more unambiguous indication of the power of direction of the *meta* alkyl groups in direct iodination.

p-Toluidine has been iodinated by elementary iodine before and only substitution *ortho* to the amino group has been recorded (Fig. 1).[3] The higher *p*-alkylanilines have not been iodinated directly, but their acetyl derivatives have been brominated and nitrated,[4] and no isomers other

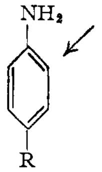

Fig. 1.

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