[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

Mechanism of Rearrangement of *N*-Alkylanilines[1]

HAROLD HART AND JOHN R. KOSAK[2,3]

Received July 19, 1961

N-α-Phenethylaniline (I), either as the hydrochloride or the zinc chloride complex, rearranged readily at 200–230° to give a mixture of *o*- and *p*-α-phenethylaniline (II_o and II_p) in moderate yield. The *ortho/para* ratio was determined by an infrared method, based on authentic samples of the two isomers, syntheses of which are described. This ratio was about 30:65 for the hydrochloride and about 10:80 for the zinc chloride complex, but independent experiments showed that zinc chloride, but not hydrogen chloride, brings about the rearrangement $II_o \rightarrow II_p$. Optically active I gives essentially racemic II.

Aniline, aniline hydrochloride, and styrene reacted at 220–230° to give good (82%) yields of II. *The product was almost exclusively the ortho isomer.* The reaction did not occur if either the aniline or its hydrochloride were omitted, nor was zinc chloride an effective catalyst. α-Phenethyl chloride and aniline, in suitable mole ratios, gave similar results.

The implications of these results for the mechanisms of the Hofmann-Martius and Reilly-Hickinbottom rearrangements are discussed.

The thermal conversion of hydrohalides of *N*-alkylanilines to ring-alkylated aniline derivatives was discovered many years ago by Hofmann and Martius[4] and the "rearrangement" bears their name.[5] Mechanistic studies were carried out by Hickinbottom and co-workers,[6–8] who also extended the reaction to Lewis-acid catalysts (a reaction now known as the Reilly-Hickinbottom rearrangement[9,10]). A few salient results of Hickinbottom's work will be outlined as background for the present study.

When *N*-alkylarylamine *hydrohalides* were heated (200–300°), the alkyl group "migrated" predominantly to the *para* position; alkyl halides and, for ethyl and higher alkyl groups, olefins were also produced. Furthermore, whereas the olefin and ring-alkylated aniline showed typical carbonium ion rearrangement of the migrating group, the alkyl halides were not rearranged. For example, the principal products from *N*-isoamylaniline hydrobromide (240–270°, one hour) were isoamylene, isoamyl bromide, and *p*-*t*-amylaniline.[6e,11] A possible exception to this generalization is *N*-*n*-butylaniline hydrobromide which gave (302°, one hour)[6e] the expected rearranged olefin, 2-butene, and unrearranged alkyl halide, *n*-butyl bromide, but gave *p*-*n*-butylaniline.[12]

In contrast to the hydrohalides, the *metal halide*-catalyzed rearrangement (ZnX_2, CoX_2, CdX_2; X = Cl, Br) did not give alkyl halides, although olefins were obtained when the alkyl group was tertiary or secondary. Most intriguing, the alkyl group in the ring-alkylated product was not isomerized. For example *N*-isoamylaniline (240–250°, seven hours, cobaltous chloride) gave *p*-isoamylaniline,[6f] and *N*-*n*-hexylaniline gave *p*-*n*-hexylaniline and *N*-*p*-di-*n*-hexylaniline.[6i]

Finally, Hickinbottom showed that aromatic amines can be alkylated by olefins in the presence of a hydrogen halide or metal halide, using the same conditions which bring about the "rearrangements." Thus aniline and trimethylethylene, with either hydrogen or cobaltous chloride, gave *p*-*t*-amylaniline.[6f]

At the time of this early work (1920–1937) it was necessary to rely largely on derivatization and physical constants (boiling point, refractive index)

---

(1) For a preliminary communication of part of this work, see H. Hart and J. R. Kosak, *J. Org. Chem.*, **22**, 1752 (1957).

(2) Taken from the Ph.D. thesis of John R. Kosak, Michigan State University, 1957.

(3) Research Corp. Fellow, 1956–1957. We appreciate the financial support of the Research Corp. for this work.

( ) A. W. Hofmann and C. A. Martius, *Ber.*, **4**, 742 (1871); A. W. Hofmann, *Ber.*, **5**, 704, 720 (1872).

(5) J. E. Gowan and T. S. Wheeler, *Name Index of Organic Reactions*, Interscience, New York, 1960, p. 126.

(6) (a) J. Reilly and W. J. Hickinbottom, *J. Chem. Soc.*, **117**, 103 (1920); (b) W. J. Hickinbottom, *J. Chem. Soc.*, 64 (1927); (c) W. J. Hickinbottom and A. C. Wayne, *J. Chem. Soc.*, 1558 (1930); (d) W. J. Hickinbottom and G. H. Preston, *J. Chem. Soc.*, 1566 (1930); (e) W. J. Hickinbottom and S. E. A. Ryder, *J. Chem. Soc.*, 1281 (1931); (f) W. J. Hickinbottom, *J. Chem. Soc.*, 946, 2396, 2646 (1932); (g) W. J. Hickinbottom, *J. Chem. Soc.*, 319, 1700, 1981 (1934); (h) W. J. Hickinbottom, *J. Chem. Soc.*, 1279 (1935); (i) W. J. Hickinbottom, *J. Chem. Soc.*, 404, 1119 (1937).

(7) See also R. W. Cripps and D. H. Hey, *J. Chem. Soc.*, 14 (1943) and other papers in that series which describe *meta* alkylation and other side reactions in the original Hofmann-Martius alkylation of anilines with methanol. A review of the early literature is included in the first paper, D. H. Hey, *J. Chem. Soc.*, 1581 (1931).

(8) J. W. Howard and C. G. Derick [*J. Am. Chem. Soc.*, **46**, 166 (1924)] carried out a quantitative study of the thermal decomposition of methylaniline hydrochloride and concluded that quaternary salt formation was essential to the reaction.

(9) Ref. 5, p. 205.

(10) For a brief review of the present status of these two reactions see C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, New York, 1953, pp. 615–618.

(11) The olefin was probably mainly 2-methyl-2-butene, judging from the reported boiling point.

(12) Identified as the acetyl derivative; the crude product also contained an isomeric "aminobutylbenzene."

TABLE I

REARRANGEMENT OF *N*-α-PHENETHYLANILINE (I)

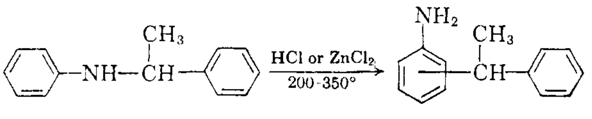
Exp. No.	I, Moles	Catalyst, Moles	Hours[a]	Temp.	% of C-Alkylate	% Isomers *ortho*	% Isomers *para*
1	0.05	—	2.5	300–315	—[b]	—	—
2	0.1	HCl, 0.1	3.0	225–230	24.0	40	48
3	0.1	HCl, 0.1	6.0	210–230	19.0	25	70
4	0.1	HCl, 0.1	6.0	220–230	22.0	32	60
5	0.2[c]	HCl, 0.2	6.0	220–230	21.1[d]	29	61
6	0.02[e]	HCl, 0.02	2.0	300–315	—[f]	—	—
7	0.1	$ZnCl_2$, 0.05	11.0	210–230	25.7	1	95
8	0.25	$ZnCl_2$, 0.25	6.0	210–220	40.7	3	90
9	0.15[g]	$ZnCl_2$, 0.15	6.0	220–230	34.0[h]	13	75
10	0.1	$ZnCl_2$, 0.1	8.0	300–310	30.4	9	84
11	0.1[e]	$ZnCl_2$, 0.1	6.0	330–350	Trace[i]	—	—
12	0.05	—	2.0	320–326	—[j]	—	—
13	0.1	HCl, 0.1	6.0	220–230	19.5[k]	—	—
14	0.075	$ZnCl_2$, 0.075	6.0	210–220	24.0[l]	—	—

[a] All reactions in sealed tubes unless otherwise stated. [b] 65% Recovery of starting material. At 210–230°, recovery of starting material was nearly quantitative. [c] $[\alpha]^{25}_{D}$ +16.6°, 1 = 1 dm., $c = 20$, $d = 0.8331$, ethanol. [d] $[\alpha]^{25}_{D}$ +0.20, 1 = 1 dm., $c = 40$, benzene. [e] Open tube. [f] Aniline hydrochloride (27%) sublimed from the tube. [g] $[\alpha]^{24}_{D}$ −17.86°, 1 = 1 dm., $c = 20$, $d = 0.8331$, ethanol. [h] Inactive. [i] The main products were aniline (57.6%) and styrene (67.5%). [j] 84.7% Recovered starting material. [k] *o*-α-Phenethyl-*p*-toluidine; in addition, 9% of *p*-toluidine was recovered. [l] *o*-α-Phenethyl-*p*-toluidine; in addition, 20% of *p*-toluidine was recovered.

to detect and prove the structures of isomers which might vary either in the skeleton of the migrating alkyl group, the position of substitution on the aniline, or both. It seemed desirable to reinvestigate certain of these reactions using modern analytical methods.[13] *N*-α-Phenethylaniline was selected for detailed study for several reasons: (a) No optically active amine had previously been rearranged, and the configurational relationships of the α-phenethyl group are well known; (b) the rearrangement was expected to be facile, as *N*-benzylaniline had been studied previously[6i] and α-phenethyl is appreciably better than benzyl in the rearrangement of the analogous ethers[14]; and (c) the alkylation of aniline with styrene, a reaction expected to yield the same products as the rearrangement, had been studied.[6g] As it turned out, studies with optically active amine were relatively uninformative, but the *ortho-para* isomer distributions in the α-phenethylanilines derived from rearrangement of *N*-α-phenethylaniline (hydrochloride or zinc chloride complex) and from alkylation of aniline with styrene place some restrictions on possible reaction mechanisms.

RESULTS

N-α-Phenethylaniline (I), *o*-α-phenethylaniline (II_o), and *p*-α-phenethylaniline (II_p) were synthesized by unambiguous routes (*vide infra*). Two bands in the infrared spectra of II_o (8.73, 10.77 μ) and II_p (8.48, 8.88 μ) permitted the development of an analytical method accurate to ±2.5 absolute percent for each isomer.[15] The results of several rearrangements are summarized in Table I.



I

II_o and II_p

Unlike α-phenethyl phenyl ether,[14] which rearranged readily at 200° to ring-alkylated phenols, its nitrogen analog I was relatively stable thermally. No change was observed at 200° and even after two hours of reflux at 300–315°, 65% of I was recovered unchanged, and little or no ring-alkylated aniline was observed. Similarly, *N*-α-phenethyl-*p*-toluidine was recovered (84%) after two hours at 320–326°. But the hydrochloride or zinc chloride complex "rearranged" readily at 210–230°, giving varying amounts of II_o, II_p, as well as some aniline and polystyrene. The zinc chloride complexes generally gave higher yields (30–40%) of II than did the hydrochlorides (20–24%), and gave less *ortho* isomer (1–13% compared with 25–40%), and more *para* isomer (75–95% compared with 48–70%). Optically active I gave essentially inactive II, either with hydrogen chloride or zinc chloride.

When the reactions were carried out in opened rather than sealed tubes (Table I, experiments 6 and 11), virtually no II was obtained; with zinc chloride,

---

[13] It should perhaps be mentioned that at the time the work on this paper was done, vapor phase chromatography was not available to us, and one might extend this comment to our work. Nevertheless, infrared analysis turned out to be a rather sensitive tool, and our results are likely to be altered only in a minor quantitative way by further refinement.

[14] H. Hart and H. S. Eleuterio, *J. Am. Chem. Soc.*, 76, 516, 519 (1954).

[15] As the sum of independent analyses at the four wave lengths varied from about 88–96%, it would seem that any *meta* isomer would not be present in amounts >5–10% and was ignored.

TABLE II

α-PHENETHYLATION OF ANILINE

Exp. No.	Aniline, Moles	Alkylating Agent,[a] Moles	Catalyst[b]	Hours[c]	Temp.	% of C-Alkylate	% Isomers *ortho*	% Isomers *para*
1	0.43	S, 0.1	—	6.0	220–230	—[d]	—	—
2	0.1[e]	S, 0.1	—	6.0	220–230	Trace[f]	—	—
3	0.43	S, 0.1	AHC, 0.06	6.0	220–230	68.6	Not determined	
4	0.43	S, 0.1	AHC, 0.06	6.0	220–230	82.2	90	5
5	0.43	S, 0.1	AHC, 0.06	1.0	220–230	36.0	Not determined	
6	0.43	S, 0.1	AHC, 0.06	2.0	140–150	—	—	—
7	0.43	S, 0.1	AHC, 0.06	6.0	220–230	64.0	95	5
8	0.21	S, 0.2	Z, 0.2	1.5	130–145	Trace	—	—
9	0.43	S, 0.4	Z, 0.4	6.0	220–230	—	—	—
10	0.30	S, 0.1	Z, 0.1	6.0	220–230	10[f]	—	—
11	0.43	PHC, 0.06	—	6.0	220–230	52.5	72	17
12	0.43	PHC, 0.1	—	6.0	220–230	62.0	70	20
13	0.43	PHC, 0.1	—	6.0	220–230	67.0	80	15
14	0.1	PHC, 0.1	—	6.0	220–230	Trace	—	—
15	0.1	PHC, 0.1	—	48.0	[g]	[h]	—	—

[a] S = styrene; PHC = α-phenethyl chloride. [b] AHC = aniline hydrochloride; Z = zinc chloride. [c] All experiments in sealed tubes unless otherwise stated. [d] 56% of the aniline was recovered, plus considerable polymer. [e] Aniline hydrochloride. [f] Mainly *para*. [g] Room temperature for several hours, then steam bath for several hours, open beaker. [h] Products were aniline hydrochloride (81%) and styrene (71%).

the main products came from elimination (aniline and styrene), and aniline hydrochloride sublimed when an open tube of I-hydrochloride was heated at 300–315°.

The higher yield of *para* isomer with zinc chloride might have resulted from further rearrangement of initially formed ortho isomer. To test this hypothesis, II$_o$-hydrochloride and II$_o$–zinc chloride complex were separately heated at 220–230° for six hours. The zinc chloride complex gave II$_p$ in 40% yield, and none of the *ortho* isomer was recovered. On the other hand the hydrochloride, although it was thermally labile (only 30% recovery of II$_o$), gave none of the *para* isomer. Thus the high yields of *para* isomer with zinc chloride are in part rationalized.

The only example previously reported to give appreciable amounts of *ortho* isomer (when the *para* position was not blocked) was the cobaltous chloride-catalyzed rearrangement of *N*-benzylaniline[6i]; I seems to be another example, particularly as the hydrochloride. *ortho* Rearrangement of *N*-α-phenethyl-*p*-toluidine (Table I, experiments 13 and 14) proceeded normally.

As elimination products—aniline hydrochloride and styrene—were obtained from open tube decompositions, whereas similar conditions in sealed tubes gave ring-alkylated anilines, it seemed desirable to investigate directly the reaction between aniline hydrochloride and styrene, and the related pair, aniline and α-phenethyl chloride. Hickinbottom had reported[6g] that a mixture of aniline and its hydrochloride reacted with styrene (200–240°, six hours, sealed tube) to give a 28.4% yield of α-phenethylanilines (26.4% *ortho*, 62.3% *para*, and 11.3% *N*). Somewhat different results were obtained when these experiments were duplicated and extended; they are summarized in Table II. Aniline or aniline hydrochloride separately was not alkylated on the ring by styrene (experiments 1 and 2), but when the two were combined, 64–82% yields of II were obtained (appreciably higher than the reported[6g] 28%).[16] *Most remarkable was the very high yield (90–95%) of ortho isomer.* A good yield (52–67%) of II, again mainly *ortho* (70–80%), was obtained when an excess of aniline was heated with α-phenethyl chloride. This was not surprising, as it was shown (experiment 15) that aniline and α-phenethyl chloride react rather rapidly at room temperature to give aniline hydrochloride and styrene in good yield.

DISCUSSION

Mechanism. The only reasonably explicit modern mechanism which has been proposed for the Hofmann-Martius rearrangement is that of Hughes[17] based mainly on earlier views of Hickinbottom.[6] Hughes considers the initial step to be an S$_N$2 displacement of the alkyl group from the anilinium ion by halide ion. In the ionic solvent (anilinium salt), the halide may ionize, and the carbonium ion thus produced may either eliminate a proton or attack the aniline ring (summarized in equations 1–4). The first step is included mainly to explain lack of skeletal isomeriziaton in the halide, but allowing *via* R$^+$ rearrangement in the olefin and alkylaniline. This mechanism, although an obvious oversimplification, can with suitable modification explain most of the facts now known about the reaction.[18]

---

(16) No effort was expended on determining optimum conditions.

(17) E. D. Hughes, as referred to by C. K. Ingold, ref. 10.

$$\mathrm{Ar\overset{+}{N}H_2R} + X^- \xrightarrow{\mathrm{S_N2}} \mathrm{R}X + \mathrm{ArNH_2} \qquad (1)$$

$$\mathrm{R}X \rightleftharpoons \mathrm{R^+} + X^- \qquad (2)$$

$$\mathrm{R^+ + ArNH_2} \rightleftharpoons \text{olefin} + \mathrm{Ar\overset{+}{N}H_3} \qquad (3)$$

$$\mathrm{R^+ + ArNH_2} \longrightarrow \mathrm{R{-}ArNH_2 + H^+} \qquad (4)$$

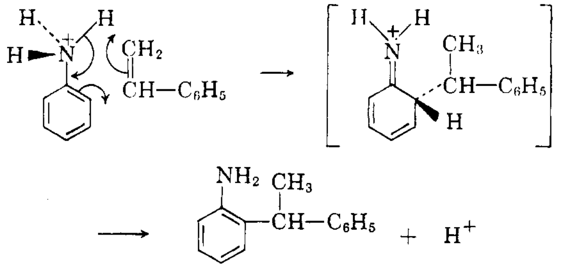
One of these modifications is the direct ionization of $\mathrm{Ar\overset{+}{N}H_2R \rightarrow ArNH_2 + R^+}$, when R is likely to produce a good carbonium ion (as suggested by Hickinbottom), as for example α-phenethyl. The present case will be considered in some detail.

The first step of the rearrangement of *N*-α-phenethylaniline hydrochloride cannot be dissociation to aniline and α-phenethyl chloride (as proposed by Hughes-Ingold) or into aniline hydrochloride and styrene. If either were the case then the yield of *C*-α-phenethylaniline from the rearrangement would be much higher than the 20–25% observed (Table I, experiments 2–5), as α-phenethyl chloride alkylated aniline in 52–67% yield (Table II, experiments 11–13) and styrene alkylated aniline hydrochloride in 64–82% yield (Table II, experiments 3, 4, 7). Furthermore, the predominant isomer in the latter two reactions was *ortho* (II_o) whereas rearrangement gave mainly the *para* isomer (II_p).

The first step is therefore most likely dissociation of *N*-α-phenethylanilinium ion into aniline and α-phenethyl cation (a direct intramolecular rearrangement is not likely in view of the large degree of racemization in the product). The latter may combine with chloride ion (not very likely), eliminate a proton to produce styrene and ultimately polystyrene, or attack the aniline ring preferentially in the electronically and sterically favored *para* position.

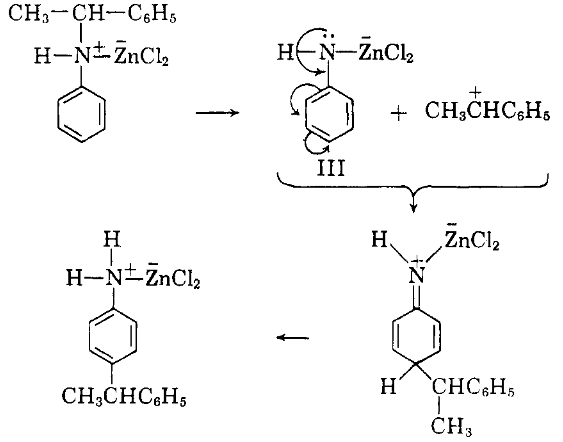
It remains to account for the remarkable specificity of *ortho* alkylation of aniline by styrene in the presence of aniline hydrochloride.[19] This cannot yet be done in detail but several features of the reaction are clear. The hydrochloride is necessary (presumably as a proton donor[20]) to the reaction, for when it is omitted alkylation does not occur (Table II, experiment 1). But equimolar amounts of hydrochloride and styrene, provided either directly (Table II, experiment 2) or indirectly as aniline and α-phenethyl chloride (Table II, experiment 14), give only a trace of product; an excess of free aniline is necessary.

When styrene is protonated by the anilinium ion, the orientation may be favorable for a mechanism such as in the scheme with an intermediate stage



(not shown) in which the benzylic carbon has considerable positive charge.[21] Separation of the α-phenethyl cation may occur, especially in ionizing solvents, giving *para* product. The failure of anilinium chloride and styrene to react in the absence of excess aniline may be due either to limited mutual solubility (unlikely) or to lack of base to accept the proton.

Rearrangement of the zinc chloride complex was somewhat different from the hydrochloride; the yield was higher, and more *para* isomer was produced. The latter could be explained by the rearrangement of the *ortho* isomer, shown to occur with zinc chloride but not with the hydrochloride. The rearrangement may proceed according to the scheme.



The intermediate III should be more susceptible to substitution than aniline itself, and, because of the size of the zinc, should favor *para* alkylation.

Syntheses. *N*-α-Phenethylaniline (I) was previously made by addition of a methyl Grignard to benzylaniline[22] and by *p*-toluenesulfonic acid-catalyzed condensation of α-phenethanol with

---

(18) An earlier π-complex mechanism suggested by M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 227 has no experimental justification.

(19) As α-phenethyl chloride was dehydrohalogenated rapidly by aniline at room temperature, it is obvious that the high yields of *ortho* isomers when this reaction is carried out in a sealed tube at high temperatures (Table II, experiments 11–13) are obtained by the same mechanism.

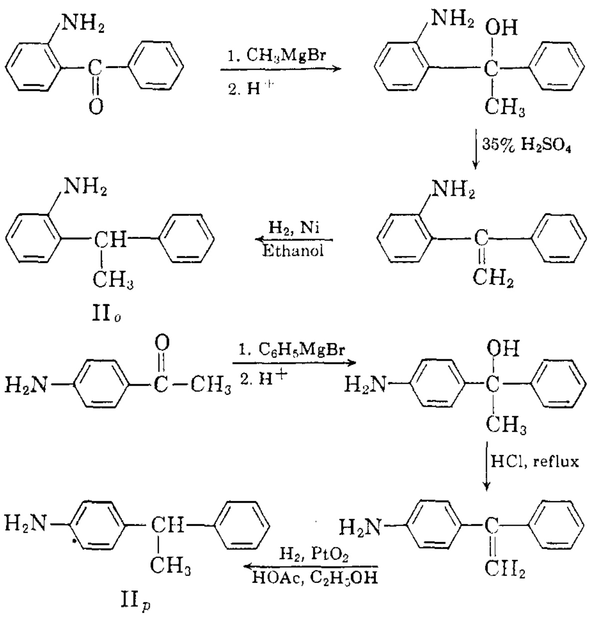
(20) The need for a proton donor is evident from the fact that zinc chloride, although it brought about rearrangement of *N*-α-phenethylaniline, could not efficiently catalyze the alkylation of aniline by styrene (Table II, experiments 8–10).

(21) A cyclic mechanism was proposed by G. G. Ecke, J. P. Napolitano, A. H. Filbey, and A. J. Kolka, *J. Am. Chem. Soc.*, 22, 639 (1957) to explain the specific *ortho* alkylation of aluminum salts of aniline by olefins.

(22) M. Busch, *Ber.*, **37**, 2691 (1904).

aniline.[23] Modification of the Willson and Wheeler[24] synthesis of *N*-benzylaniline gave I in 60–82% yield. The method consists of allowing aniline, α-phenethyl chloride, and sodium bicarbonate to react for several hours at 25–98°. Unfortunately, when optically active α-phenethyl chloride was used, the product was racemic. It was necessary, therefore, to resolve *dl*-I; the method of Descamps[23] worked well.

Authentic samples of II_o and II_p were synthesized according to the schemes shown. No difficulties were encountered in the synthesis of II_o. In the synthesis of II_p, dehydration of the tertiary carbinol with 35% sulfuric acid (as with II_o) lead to an as yet unidentified sulfur-containing compound m.p. 217–218° (not amine sulfate). The dehydration worked well with refluxing dilute hydrochloric acid. Also, the final hydrogenation did not work well using nickel and ethanol (the conditions used to make II_o). The reduction did proceed well using platinum and ethanol acidified with a little acetic acid.



EXPERIMENTAL[25]

N-α-Phenethylaniline (I). A mixture of 93 g. (1.0 mole) of aniline, 29.4 g. (0.35 mole) of sodium bicarbonate, 50 ml. of water, and 35 g. (0.25 mole) of α-phenethyl chloride was heated at 95–98° with vigorous stirring for 4 hr., cooled, filtered, and the layers separated. The organic layer was washed with three 50-ml. portions of saturated salt solution, dried over sodium sulfate, and distilled, giving 65 g. (69.9%) of recovered aniline, b.p. 50–55° at 1 mm., and 34.7 g. (71% based on chloride) of *N*-α-phenethylaniline, b.p. 132–134° at 1 mm., hydrochloride, m.p 160–161.5° (lit.[22,26] m.p. 184–185°), sulfate, m.p. 140–141° (lit.[22] m.p. 142–143°), *N*,*N*′-diphenyl-*N*-(α-phenethyl)urea, m.p. 91–91.5° (lit.[22] m.p. 94–95°). On standing in the refrigerator for 2 days, a twice-distilled sample of the amine solidified, m.p. 24–25° (lit.[23] m.p. 26.4°).

The yield was improved to 81.4% simply by allowing the reaction to proceed at room temperature for 6 hr. Sodium carbonate may replace the bicarbonate without effect on yield. Optically active α-phenethyl chloride (α_D^{27} −34.6, 1 = 1 dm.) gave racemic product. Optically active I was obtained by resolution of the *dl*-amine using the procedure of Descamps.[23]

N-α-Phenethyl-p-toluidine. The procedure was the same as that described above for the corresponding aniline. The yield (same scale) of *N*-α-phenethyl-*p*-toluidine, m.p. 68–68.5° from ethanol (lit.[6g] m.p. 69–70°) was 62.6%; *N*-(α-phenethyl)-*N*-(*p*-tolyl)-*N*′-phenylurea, m.p. 89–90°.

Anal. Calcd. for $C_{22}H_{22}N_2O$: C, 80.0; H, 6.67. Found: C, 79.7; H, 6.57.

o-α-Phenethylaniline (II_o). *o*-Aminobenzophenone[27] was converted with excess methylmagnesium iodide to 1-phenyl-1-*o*-aminophenylethanol, crude m.p., 80–83° (lit.[28] m.p. 84–85°) in 64% yield. The crude carbinol was dehydrated with sulfuric acid[28] giving 1-(*o*-aminophenyl)-1-phenylethylene, m.p. 81.5–82° (lit.[28] m.p. 76–77.5) in 51% yield. The olefin (5.85 g., 0.03 mole) in 100 ml. of absolute ethanol was hydrogenated in 1 hr. at room temperature and 3 atm. pressure over 2 g. of Raney nickel to give, after recrystallization from ethanol, 3.5 g. (60%) of *o*-α-phenethylaniline, m.p. 58.5–59° (lit.[6g] m.p. 58–59°); hydrochloride, m.p. 155–157°.

p-α-Phenethylaniline (II_p). 1-Phenyl-1-*p*-aminophenylethanol was prepared in 62% yield from 1 mole of phenylmagnesium bromide and 0.25 mole of *p*-aminoacetophenone. The product, m.p. 103.5–105° compared with that obtained[29] from 4-aminobenzophenone and methyl Grignard, m.p. 101°.

The carbinol (33 g.) was dehydrated by refluxing for 1 hr. with 100 ml. of dilute (1:4) hydrochloric acid. The cooled solution was poured into 200 ml. of ice cold 5% sodium hydroxide. The brown solid which separated was recrystallized from petroleum ether (b.p. 30–60°) to give 16 g. (53%) of 1-(*p*-aminophenyl)-1-phenylethylene, m.p. 79.5–80°.

Anal. Calcd. for $C_{14}H_{13}N$: C, 86.15; H, 6.67. Found: C, 86.13; H, 6.82.

The olefin (5.85 g., 0.03 mole) in 100 ml. of absolute ethanol and 4 ml. of glacial acetic acid, with 0.2 g. of platinum oxide, was hydrogenated in 3 hr. at 3 atm. pressure and room temperature. The mixture was poured into 100 ml. of cold 5% sodium hydroxide and extracted with benzene. After drying (potassium carbonate) and distillation there was obtained 3.8 g. (65%) of *p*-α-phenethylaniline (II_p) b.p. 165–168° at 3 mm., acet-(*p*-α-phenethyl)anilide m.p. 108–109° (lit.[6g] m.p. 112–113°).

Analysis of mixtures. Mixtures of II_o and II_p were analyzed by infrared (Perkin-Elmer Model 21, sodium chloride 0.5-mm. cells). Characteristic bands at 8.73 and 10.77 μ in II_o and 8.48 and 8.88 μ in II_p were used. Suitable calibration curves were prepared with known mixtures of authentic II_o and II_p, and the method, tested with "unknowns," was shown to be accurate to ±2.5 absolute per cent.

Thermal rearrangement of I. I (19.7 g., 0.1 mole) was heated in a Claisen flask at 300–315° for 2 hr., during which time 1 g. of aniline distilled. Fractionation gave 12 g. (60%)

---

[23] R. Descamps, *Bull. soc. chim. Belges*, **33**, 269 (1924).

[24] F. G. Willson and T. S. Wheeler, *Organic Syntheses*, Coll. Vol. I, 102 (1941).

[25] Analyses by Clark Microanalytical Laboratory, Urbana Ill.

[26] The reason for the discrepancy is not known; all other constants check well.

[27] H. J. Scheifele, Jr., and D. F. DeTar, *Organic Syntheses*, *32*, 8 (1952).

[28] R. Stoermer and H. Fincke, *Ber.*, **42**, 3119 (1909).

[29] C. W. Porter and C. T. Hirst, *J. Am. Chem. Soc.*, **41**, 1265 (1919).

of recovered starting material and some polystyrene. I was stable to heat at 200°.

In a similar experiment, 10.5 g. (0.05 mole) of *N*-α-phenethyl-*p*-toluidine gave, after 2 hr. at 320–326°, 8.9 g. (84.7%) of recovered starting material and 0.15 g. of unidentified product, b.p. 210–212° at 2 mm.

Rearrangement of I-*hydrochloride. Sealed tube.* The hydrochloride (23.3 g., 0.1 mole) was heated in a sealed Pyrex tube at 200–230° for 6 hr. On cooling, the contents were extracted with dilute (1:1) hydrochloric acid and ether. The ether layer was extracted (2 × 50 ml.) with 1:1 hydrochloric acid. The ether layer, after drying (potassium carbonate) and distillation, gave 3 g. of glass-like semisolid (polystyrene?). The combined acid extracts were neutralized with 5% sodium hydroxide, extracted with benzene, dried, and distilled to give[30] 2.3 g. of aniline and 4.7 g. (24%) of a mixture of *o*- and *p*-α-phenethylanilines, b.p. 165–170° at 3 mm. containing 25–32% II$_o$ and 60–70% II$_p$ by infrared analysis (*vide supra*). There was also 2 g. of higher boiling amine residue.

Results of similar experiments are summarized in Table I.

In a similar manner, *N*-α-phenethyl-*p*-toluidine (34.6 g., 0.1 mole) gave after 6 hr. at 220–230° 3.0 g. of *p*-toluidine, 4.1 g. (19.5%) of *o*-(α-phenethyl)*p*-toluidine and 11.0 g. of an acid-insoluble glass.

Open tube. When I-hydrochloride was heated in an open tube at reflux for 1 hr., aniline hydrochloride sublimed from the reaction mixture and was collected in 27% yield.

Rearrangement of I *with zinc chloride.* I (19.7 g., 0.1 mole) and anhydrous zinc chloride (13.6 g., 0.1 mole) were heated in a sealed Pyrex tube at 220–230° for 6 hr. The cooled contents of the tube were digested on the steam bath with 100 ml. of 10% sodium hydroxide. The mixture was extracted with ether (3 × 100 ml.) and the combined ether layers extracted with 1:1 hydrochloric acid (4 × 100 ml.). The combined acid extracts were neutralized with 5% sodium hydroxide, extracted with benzene, dried (potassium carbonate), and distilled[31] to give 3.6 g. of aniline, 6.8 g. (41%) of a mixture of 3–13% II$_o$, 75–90% II$_p$, and 2.0 g. of higher boiling product. The acid-insoluble fraction gave 2 g. of polymer.

Results of similar experiments are summarized in Table I.

In a similar reaction, *N*-α-phenethyl-*p*-toluidine (15.8 g., 0.075 mole) and zinc chloride (9.8 g., 0.075 mole) gave after 6 hr. at 210–220° 2.9 g. of *p*-toluidine and 3.8 g. (24%) of *o*-α-phenethyl-*p*-toluidine, b.p. 192–200° at 8 mm. Reaction of the latter with phenyl isocyanate gave the corresponding urea, m.p. 194–195° from aqueous ethanol.

Anal. Calcd. for $C_{22}H_{22}N_2O$: C, 80.0; H, 6.67. Found: C, 79.8; H, 6.82.

When the reaction was carried out with I and zinc chloride in an open Claisen flask at 330–350°, styrene (identified as its dibromide, m.p. 72–73°) was collected as distillate in 67.5% yield. The residue gave 57.6% recovered aniline and 15.7% of glass-like acid-insoluble polymer.

Reaction of aniline, aniline hydrochloride, and styrene. A mixture of aniline (40 g., 0.43 mole), styrene (10.8 g., 0.1 mole), and aniline hydrochloride (8 g., 0.06 mole) was heated in a sealed tube at 220–230° for 6 hr. Work-up according to Procedure A[30] gave 25.7 g. of recovered aniline and 16.2 g. (82% based on styrene) of α-phenethylaniline(5% II$_p$, 90–95% II$_o$). The neutral product was 7 g. of polymer. Results of similar experiments are summarized in Table II.

Reaction of aniline with styrene. A mixture of styrene (10.8 g., 0.1 mole) and aniline (40 g., 0.43 mole) was heated in a sealed tube at 200–230° for 6 hr. Work-up (procedure A) gave 22.5 g. of recovered aniline and 20 g. of neutral polymer (note: this must include some polymer derived from aniline).

Reaction of aniline hydrochloride with styrene. A mixture of aniline hydrochloride (12.95 g., 0.1 mole) and styrene (10.4 g., 0.1 mole) was heated in a sealed tube at 220–230° for 6 hr. Work-up (procedure A) gave 7.2 g. (77.4%) of recovered aniline and a trace (0.3 g.) of higher boiling amine.

Reaction of aniline, styrene, and zinc chloride. A mixture of aniline (40 g., 0.43 mole), anhydrous zinc chloride (54.4 g., 0.40 mole), and styrene (41 g., 0.40 mole) was heated in a sealed tube at 220–230° for 6 hr. Work-up (procedure B) gave 31 g. of recovered aniline, 36 g. of brittle neutral polymer. From a similar experiment using 0.1 mole each of styrene and zinc chloride and 0.3 mole of aniline there was isolated a small yield (2 g.) of α-phenethylaniline, mainly II$_p$.

Reaction of aniline with α-phenethyl chloride. Room temperature. Aniline (9.3 g., 0.1 mole) and α-phenethyl chloride (14 g., 0.1 mole) were allowed to react in an open beaker at room temperature for several hours (solid formed after 1 hr.). The solid was filtered and washed with benzene, yielding 6 g. of aniline hydrochloride. The filtrate was warmed for a few hours on the steam bath and filtered giving additional aniline hydrochloride (total yield 10.5 g., 81%). The filtrate was extracted with 1:1 hydrochloric acid, dried over potassium carbonate, the solvent removed and the residue dissolved in carbon tetrachloride and treated with bromine. There was obtained 18.8 g. (71.2%) of styrene dibromide, m.p. and mixed m.p. 72–73°.

High temperature. A mixture of 40 g. (0.43 mole) of aniline and 14 g. (0.1 mole) of α-phenethyl chloride was heated in a sealed tube at 220–230° for 6 hours. Work-up (procedure A) gave 19.5 g. of recovered aniline and 13.2 g. (67%) of α-phenethylaniline (15–20% II$_p$, 70–80 II$_o$). A neutral glass-like polymer, 6.3 g., was also obtained.

Isomerization of II$_o$. A mixture of 0.8 g. of II$_o$-hydrochloride and 3.3 g. of free amine (II$_o$) was heated in a sealed tube at 220–230° for 6 hr. Work-up (procedure A) gave 1.2 g. of recovered amine, b.p. 140–155° at 1 mm. which, from the infrared spectrum, was free of II$_p$. Also 1.5 g. of neutral polymer was obtained.

When 9.9 g. (0.05 mole) of II$_o$ and 6.8 g. (0.04 mole) of anhydrous zinc chloride were heated in a sealed tube at 220–230° for 4 hr., then worked up (procedure B), there were obtained 4.0 g. (40%) of II$_p$, 1.6 g. of higher boiling amine and 2.2 g. of neutral polymer.

EAST LANSING, MICH.

---

[30] This will be referred to as work-up Procedure A.

[31] This will be referred to as work-up Procedure B.