

Photochemical Reactions of N-Alkylanilines¹

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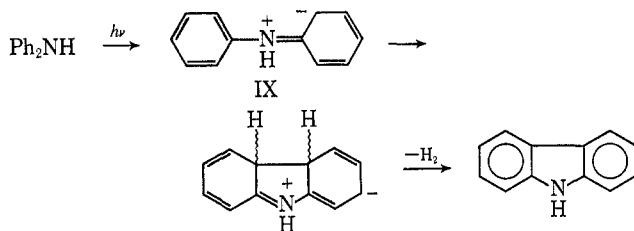
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Ultraviolet irradiation of N-phenylbenzylamine (Ia) and N- α -phenethylamine (Ib) in various solvents gave *ortho*- and *para*-alkylated anilines in yields of 5.5–42.5% together with aniline and coupling products of alkyl radicals (V). The *ortho/para* ratio is 2–8, and it rises to *ca.* 20 in the presence of radical scavenger, hydroquinone. No rearrangement of *ortho* to *para* occurs. The irradiation of a mixture of N-phenylbenzylamine (Ia) and N-(*o*-tolyl)- α -phenethylamine (Id) gave no cross-bred products at N and *ortho* positions. With optically active N- α -phenethylamine (VI), appreciable optical activity was retained in recovered VI and in both *ortho* (VII) and *para* isomers (VIII). On the other hand, addition of hydroquinone to the reaction system results in a *ca.* twofold increase of the optical activity of VIII. The reaction mechanism is discussed on the basis of these data.

Thermal rearrangement of N-monoalkylaniline hydrochlorides in a sealed tube to give ring-alkylated anilines has long been known as the Hofmann–Martius rearrangement,^{2,3} while the photochemical secondary processes of aromatic amines have little been investigated, and no report is thus far available on the photorearrangement of N-alkylanilines.

N,N-Dimethylaniline itself is quite stable under ultraviolet (uv) light.⁴ The N,N-dimethylaniline hydrochloride can be photolyzed,⁴ but the rearrangement to ring-alkylated aniline has not been observed. Diphenylamines have been reported to be photolyzed to carbazoles through an intramolecular charge-separated species (IX) followed by the ring formation at *ortho* positions.⁵



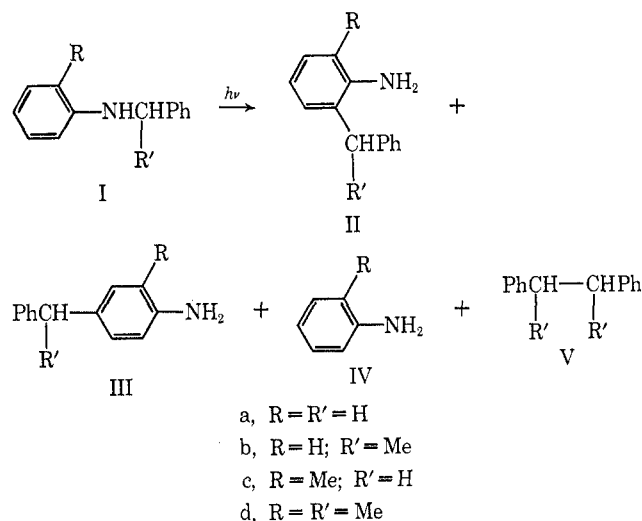
The present paper describes a novel rearrangement of N-monoalkylanilines involving an alkyl–N bond fission to ring-alkylated anilines by uv irradiation, *i.e.*, photochemical Hofmann–Martius rearrangement of N-phenylbenzylamine (Ia) and N- α -phenethylamine (Ib).

Results and Discussion

The Photolysis of N-Alkylaniline.—The uv irradiation of 0.1 M solution of 1:1 isopropyl alcohol–*t*-butyl alcohol containing N-phenylbenzylamine (Ia) under nitrogen atmosphere by a high press Hg lamp (Halos, 300 W) for 20 hr gave *o*- (IIa) and *p*-aminodiphenylmethanes (IIIa) in yields of 28.9 and 13.6%, respectively, together with decomposition products, aniline (5.8%) and

bibenzyl (3.0%). The quantum yield of disappearance of Ia was *ca.* 0.48. This photorearrangement occurs also in other solvents, *e.g.*, benzene and *t*-butyl alcohol (Table I).

In a similar manner, irradiation of N- α -phenethylamine (Ib) also gave *o*- α -phenethylamine (IIb, 26.1%) and *p*- α -phenethylamine (IIIb, 8.1%), aniline (IV, 8.4%), and 2,3-diphenylbutane (Vb, 1.9%). The re-



arranged products (IIa and IIIa) isolated by means of chromatography on a 15 × 300 mm column, slurry packed with 100 mesh silica gel (Mallinckrodt) in benzene, were identified with corresponding authentic samples by means of glpc, melting point, and ir and uv spectra. Further, all of these products were estimated by glpc. The *para* isomer is not formed by the rearrangement of the *ortho* isomer as confirmed in our hands, and hence the *ortho/para* ratio was approximately constant in a range of 2.4–3.7 during irradiation time of 6–20 hr.

In the photolysis of Ia and Ib, the main product is their *ortho* isomer, *i.e.*, the *ortho/para* ratio is *ca.* 2–3, indicating that these reactions may go through an intramolecular pathway.

Photolysis of a mixture Ia and Id gave Ia, IIa, IIIa, Id, IIb, and IIIb as products, but no cross-bred product such as Ib, Ic, or Iic was detected. N cross-bred products (Ib and Ic) and an *ortho* cross-bred product (Iic) were not formed at all. Their identity was established by comparison of their retention times by glpc of the photo cross-bred products with those of authentic samples and/or photolysates of Ib, Ic, and Id. IIb,

(1) Contribution No. 135.

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TABLE I
 YIELDS^a OF PHOTOPRODUCTS FROM N-PHENYLBENZYLAMINE (Ia) AND N- α -PHENETHYLANILINE (Ib)

Reactant ^b	Solvent	Additive	Conversion	%			ortho/para
				ortho product II	para product III	Aniline (IV)	
Ia	Mixed solvent ^c		55.4	28.9	13.6	5.8	2.1
	<i>t</i> -Butyl alcohol		54.2	11.6	1.5	6.9	7.7
	Benzene		53.8	4.8	0.7	4.8	7.3
	Mixed solvent ^c	Oxygen	47.0	10.6	1.6	5.1	6.5 ^d
	<i>t</i> -Butyl alcohol	Oxygen	59.2	11.0	1.2	12.8	7.3 ^e
	<i>t</i> -Butyl alcohol	Naphthalene	52.2	11.5	1.6	1.6	8.6
Ib	Mixed solvent ^c	Hydroquinone	74.5	18.9	0.9	9.8	20.7
	Mixed solvent ^c		57.2	26.0	8.1	8.4	3.2

^a Yields based on the consumed substrates. ^b Irradiation for 20 hr with a 300-W high press Hg lamp. ^c Isopropyl alcohol-*t*-butyl alcohol 1:1 (v/v). ^d Benzylideneaniline (1.1%) was formed as a by-product. ^e Benzylideneaniline, 6.0%.

 TABLE II
 YIELDS^a OF PHOTOPRODUCTS FROM OPTICALLY ACTIVE N- α -PHENETHYLANILINE (VI)

Reactant	Solvent	Additive	Conversion	%		ortho/para
				ortho product VII	para product VIII	
VI	Mixed solvent ^b		71.4	27.1	19.0	1.4
	Mixed solvent ^b		63.6	24.5	13.6	1.8
	Mixed solvent ^b	Hydroquinone	81.7	20.6	12.9	1.6

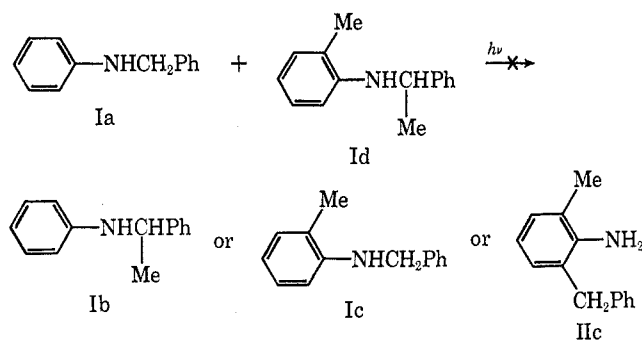
^a Based on isolated products by means of column chromatography. ^b Isopropyl alcohol-*t*-butyl alcohol 1:1 (v/v).

 TABLE III
 PHOTOREARRANGEMENT OF OPTICALLY ACTIVE N- α -PHENETHYLANILINE (VI)

Additive	Rotation ^a of recovered VI, degree	Rotation ^a of rearranged products, degree	
		ortho product VII	para product VIII
Hydroquinone	-18.4 \pm 0.6 ^b	+4.7 \pm 0.5 ^e	-3.7 \pm 0.6 ^d
	-22.3 \pm 2.1 ^c	+3.9 \pm 1.5 ^f	-0.9 \pm 1.8 ^g
	-19.8 \pm 1.0 ^h	+1.6 \pm 0.6 ⁱ	-0.6 \pm 1.3 ^j

^a The values of $[\alpha]^{25D}$ were measured in ethyl alcohol. The figures following \pm mean mechanical errors caused by ORD recorder. ^b *c* 1.74, *l* 0.2. ^c *c* 1.18, *l* 0.2. ^d *c* 0.80, *l* 0.2. ^e *c* 2.42, *l* 0.1. ^f *c* 1.02, *l* 0.1. ^g *c* 0.57, *l* 0.1. ^h *c* 1.01, *l* 0.1. ⁱ *c* 1.01, *l* 0.5. ^j *c* 0.63, *l* 0.5.

IIIb, and IIIc were not detectable by glpc on account of the overlap of glpc peaks of IIb to Ia, IIIb to IIIa, and IIIc to IIId.



The photolysis of Ia in the presence of equimolar hydroquinone gave *ca.* 20 times as much *ortho* isomer as *para* isomer, which is probably caused by trapping the intermediary alkyl radical and hence the suppression of *para*-isomer formation. This indicates that the *para* isomer may be formed by two processes, *i.e.*, intra- and intermolecular processes, and the *para* isomer is more favorably produced by the latter process than the *ortho* isomer.

The Photolysis of Optically Active N- α -Phenethyl-aniline (VI).—Optically active N- α -phenethyl-aniline (VI) (*l* form) was separated from Ib (*dl* form) as a salt of camphor- β -sulfonic acid. The salt, after being recrystallized from benzene, contains *ca.* 80% optically

pure *l* form, $[\alpha]^{25D} + 83.9^\circ \pm 1.0^\circ$ (10% solution in absolute ethyl alcohol) {lit.⁶ $[\alpha]^{20D} + 104^\circ 68'$ (10% solution in absolute ethyl alcohol)}. Optically active N- α -phenethyl-aniline (VI, *l* form), $[\alpha]^{25D} - 26.1^\circ \pm 0.9^\circ$ (2.1% solution in absolute ethyl alcohol), was obtained by its treatment with aqueous barium hydroxide. A solution of 1:1 isopropyl alcohol/*t*-butyl alcohol containing 0.66 g of VI was irradiated for 30 hr. The reaction mixture, after condensation *in vacuo*, was separated by chromatography on silica gel, where benzene-3% acetone eluted the following products in the following order: 242.1 mg of the recovered N- α -phenethyl-aniline (VI), 102.4 mg (24.5%) of *o*- α -phenethyl-aniline (VII), 56.8 mg (13.6%) of *p*- α -phenethyl-aniline (VIII), and aniline (IV) (Table II). Each fraction was identified by uv, ir, and glpc. Optical rotations of the photoproducts in ethyl alcohol follow: VI, $[\alpha]^{25D} - 22.3^\circ \pm 2.1^\circ$; VII, $+3.9^\circ \pm 1.5^\circ$; VIII, $-0.9^\circ \pm 1.8^\circ$ (Table III).

These facts show that recovered N- α -phenethyl-aniline (VI) and both the *ortho*-rearranged product VII and the *para* isomer VIII retain some optical activity. In conclusion, the photorearrangement of VI to VII and VIII is, partially at least, intramolecular. Hart, *et al.*,^{2b} have reported that the thermal rearrangement of optically active VI with hydrochloric acid or zinc chloride gave essentially racemic VII (13%) and VIII (75%). Furthermore, the intermolecularity of the rearrangement was proposed in view of the predominant

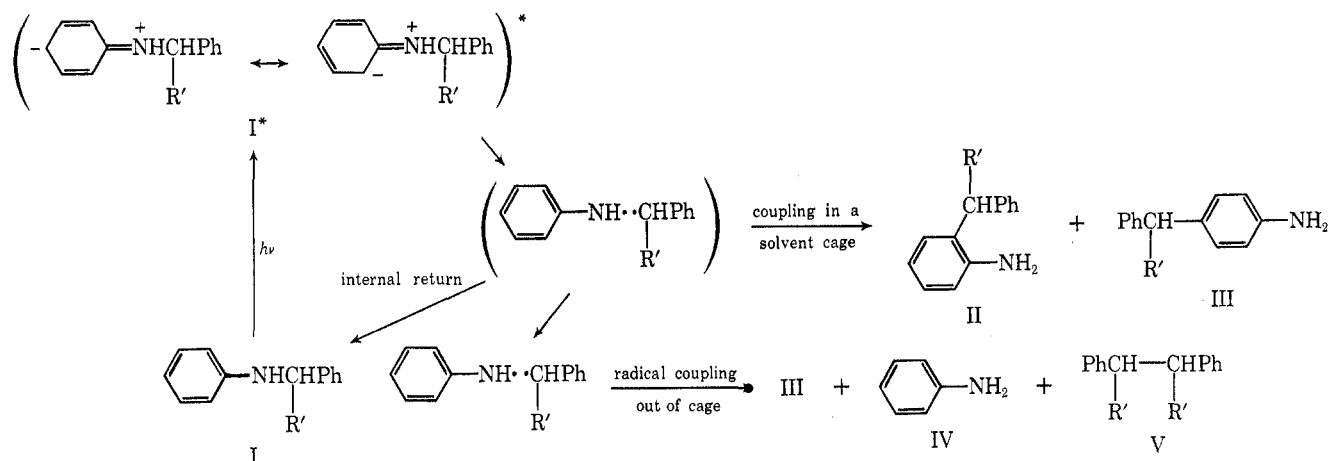
(6) R. Descamps, *Bull. Soc. Chim. Belg.*, **33**, 269 (1924); *Chem. Abstr.*, **18**, 2879 (1924).

para rearrangement (*ortho/para* ratio of 1:2–1:6), which is in contrast to the ratio of *ca.* 2 in this photorearrangement. On the contrary, thermal rearrangement of optically active α -phenethyl phenyl ether gives *o*- and *p*- α -phenethylphenols (in an *ortho/para* ratio of 85:15), both of which are also optically active.⁷

Irradiation of optically active VI in the presence of a radical scavenger, hydroquinone, gave optically active *ortho*- and *para*-rearranged products; *i.e.*, similarly, column chromatography of the reaction mixture gave 100.5 mg of recovered *N*- α -phenethylaniline (VI), $[\alpha]^{25D} -19.8^\circ \pm 1.0^\circ$, 101.0 mg of *ortho* isomer, $[\alpha]^{25D} +1.6^\circ \pm 0.6^\circ$, and 63.0 mg of *para* isomer, $[\alpha]^{25D} -6.0^\circ \pm 1.3^\circ$.

As shown in Table III, the *para*-rearranged product retained some optical activity, more than that in the reaction without hydroquinone, whereas recovered *N*- α -phenethylaniline was always optically pure, when compared with the original *N*- α -phenethylaniline (VI), within experimental error; this is in accordance with the absence of *N* cross-bred products. *o*- α -Phenethylaniline was a little less optically pure in the presence of hydroquinone than without it, probably because of contamination of some other materials. Essentially, both of *N*- α -phenethylaniline and the *ortho* isomer may be unaffected by the presence of hydroquinone.

These results suggest the following reaction scheme for the photorearrangement.



Generally, *N*-alkylanilines absorb uv light at 243–248 $m\mu$ ($\epsilon \sim 12,000$) and 291–296 (~ 2000); the former is attributable to the transition of ${}^1B_{1u} \leftarrow {}^1A_{1g}$ (probably the transition to intramolecular charge-separated species) and the latter to ${}^1B_{2u} \leftarrow {}^1A_{1g}$. On irradiation of *ca.* 250- $m\mu$ light, *N*-alkylanilines (I) are subject to cleavage into anilino and alkyl radicals *via* the above intramolecular charge-separated species (I*), whose *N*-alkyl bond is liable to scission on account of a decrease of electron density at the nitrogen position. The radicals then couple with the anilino radical at the position with high density of odd electron to form I, II, and III.

Shizuka⁸ studied the secondary processes of the photochemical rearrangement of *para*-substituted acetanilides to *o*-acetylaniline, and estimated the very high recombination quantum yields (*ca.* 0.9 in cyclohexane) of anilino and acetyl radicals. This effect is attributable

to a solvent cage effect. It is conceivable that photorearrangement of I occurs mostly in a solvent cage and only partially out of the cage, because a solvent (isopropyl alcohol-*t*-butyl alcohol) more viscous than cyclohexane is used in our reaction. Furthermore, the liberated anilino radical, which causes hydrogen bonding with surrounding hydroxy compounds, migrates out of the solvent cage with difficulty; the subsequent internal return of the two radicals gives the starting material without loss of stereochemical configuration. In addition, it is less probable that the alkyl radical has a chance to couple with another alkyl radical out of the solvent cage.

The hydroxylic solvents seem to favor the rearrangement (Table I). This solvent effect is not due to the viscosity effect, since there is no correlation of the yields with solvent viscosities. Therefore, the pronounced solvent effect on the yield of *ortho* and *para* isomers may be explained as follows. (i) Solvent hydrogen bonded to the nitrogen atom of *N*-alkylaniline may accelerate the C–N bond scission and the effect of hydroxylic solvent on quinoid form, formed in the subsequent step, also facilitate the rearrangement. This speculation is not inconsistent with the observed orientation of other photochemical rearrangements. It has been reported that the formation of *ortho* and *para* isomers in photochemical Fries rearrangement of aryl esters is more favorable in polar solvents than in nonpolar.⁹ Similar

solvent effect has been observed in the photochemical rearrangements of aryl ethers¹⁰ and benzyl methyl ketone.¹¹ (ii) The hydrogen atom donating ability of the solvent is also important. This effect may be interpreted tentatively in terms of hydrogen abstraction of the resulting alkyl radical. The migrating alkyl radical should interact more with hydrogen-donating solvents as the radical is more apart from the anilino radical; hence the ratio of *ortho/para* decreases with increasing hydrogen-donating ability of the solvent.

Experimental Section

All melting points and boiling points are uncorrected. Infrared spectra were obtained by the method of liquid film on a Perkin-Elmer grating infrared spectrophotometer, Model 337, ultraviolet spectra on a Shimadzu auto ultraviolet spectrophotometer, Model SV-50A, and optical rotation on a Jasco optical

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rotatory dispersion spectrophotometer, Model ORD/UV-5. Quantitative analysis of photolysates was done by a Yanagimoto gas chromatography with a flame ionization detector, Model GCG-550F, employing a 1.7 m \times 2.5 m column packed with PEG 20M (2.5 wt %) on Chamelite CS of 80-100 mesh using N₂ as a carrier gas at 160 to 250°.

Materials.—N-Phenylbenzylamine (Ia) was prepared by heating (at 90-95°) aniline with benzyl chloride in aqueous sodium bicarbonate: bp 158-163° (5 mm) [lit.¹² bp 178-180° (12 mm)]; mp 36.5-37° (lit.¹² mp 36°); $\lambda_{\text{max}}^{\text{MeOH}}$ 247 m μ (log ϵ 4.08) and 296 (3.25); ν_{max} (Nujol) 3410 (-NH), 1320 (C-N), and 1270 cm⁻¹ (C-N). Other N-alkylanilines (Ib, Ic, and Id) were prepared similarly: N- α -phenethylamine (Ib), bp 129° (3 mm) [lit.^{2a} bp 132-134° (1 mm)], $\lambda_{\text{max}}^{\text{MeOH}}$ 247 m μ (log ϵ 4.10) and 296 (3.23), from aniline and α -chloroethylbenzene; N-(*o*-tolyl)benzylamine (Ic), bp 138-145° (4 mm), mp 59.0-60.3°, $\lambda_{\text{max}}^{\text{MeOH}}$ 244.5 m μ (log ϵ 4.09) and 293 (3.33), from *o*-toluidine and benzyl chloride; and N-(*o*-tolyl)- α -phenethylamine (Id), bp 137-139° (4 mm), $\lambda_{\text{max}}^{\text{MeOH}}$ 243.5 m μ (log ϵ 4.11) and 291 (3.37), from *o*-toluidine and α -chloroethylbenzene. *o*-Aminodiphenylmethane (IIa) was prepared by reduction of *o*-nitrodiphenylmethane obtained from the Friedel-Crafts reaction of *o*-nitrobenzyl chloride with benzene: bp 153-155° (2 mm) [lit.¹³ 172-173° (12 mm)], $\lambda_{\text{max}}^{\text{MeOH}}$ 234 m μ (log ϵ 3.87) and 288 (3.29). *p*-Aminodiphenylmethane (IIIa) was prepared by tin reduction of *p*-nitrodiphenylmethane: bp 142-144° (1 mm), mp 33-4.5° (lit.³ mp 34-35°), $\lambda_{\text{max}}^{\text{MeOH}}$ 240 m μ (log ϵ 4.03) and 292 (2.93). *o*- and *p*- α -phenethylamines (IIb and IIIb) were prepared by the rearrangement of *N*- α -phenethylamine hydrochloride.² The mixture of *o*- and *p*- α -phenethylamines, bp 135-136° (5 mm), was chromatographed on a 15 \times 300 mm column packed with 100 mesh silica gel in benzene to separate *o*- and *p*- α -phenethylamines (IIb and IIIb). The former on recrystallization from benzene, gave white crystals (IIb): mp 57.5-58.5° (lit.^{2a} mp 58.5-59°); $\lambda_{\text{max}}^{\text{MeOH}}$ 234 m μ (log ϵ 3.87) and 288 (3.29); ν_{max} 3440, 3350 (-NH₂) and 750 cm⁻¹ (4 H). The latter was eluted as an oil (IIIb): $\lambda_{\text{max}}^{\text{MeOH}}$ 240 m μ (log ϵ 4.12) and 289 (3.12); ν_{max} 3430, 3340, 3200 (-NH₂), and 830 cm⁻¹ (2 H). Bibenzyl (Va), mp 51.3-51.8° (lit.¹⁴ mp 51-52°), was prepared by the Friedel-Crafts reaction of benzene with 1,2-dichloroethane,¹⁴ and 2,3-diphenylbutane (Vb), mp 123-124° (lit.¹⁵ mp 125-126°), by the Grignard reaction of α -bromoethylbenzene.¹⁵

Optically Active N- α -Phenethylamine (VI).—Freshly distilled *dl*-N- α -phenethylamine (14 g, 0.07 mol) was heated at 80° with camphor- β -sulfonic acid (15 g, 0.1 mol) to give a dark solution, from which the salt of *l*-amine was precipitated. The precipitate, on recrystallization, yielded 8.5 g of the salt of *l*-amine, $[\alpha]_{\text{D}}^{25} + 83.9^\circ \pm 1.0^\circ$ (*c* 1.00 g/10 cc, ethyl alcohol, *l* 0.1 dm) {lit.⁶ $[\alpha]_{\text{D}}^{25} + 104^\circ$ 68' (10% ethyl alcohol solution)}, which, on treatment with excess barium hydroxide, gave free amine (3.5 g) which after recrystallization showed mp 47.5-48.1° (lit. mp 49.2° for *l*-form,⁶ mp 26.4° for *dl* form^{2a}), $[\alpha]_{\text{D}}^{25} - 26.1^\circ \pm 0.9^\circ$ (*c* 0.215 g/10 cc, ethyl alcohol, *l* 0.1 dm).

General Procedure.—All experiments were carried out in a cylindrical quartz vessel (20 \times 150 mm) under a nitrogen atmosphere, except for preparative experiments. A Halos high press 300-W Hg lamp with a water-cooling quartz jacket was used as a light source.

A solution (0.1 M) of ca. 0.6 g of N-alkylaniline (I) in 1:1 isopropyl alcohol-*t*-butyl alcohol (30 ml) were placed in the quartz vessel, which together with the lamp was immersed in running water at 15-25° for 20 hr. A reaction mixture was evaporated under reduced pressure either to determine the yield by means of glpc or to isolate products.

A Typical Procedure for the Photolysis of N-Phenylbenzylamine (Ia).—A solution of isopropyl alcohol-*t*-butyl alcohol (300 ml) containing Ia (3.83 g) was irradiated under nitrogen gas for 30 hr. The concentrated reaction mixture was chromatographed on a 15 \times 300 mm column, slurry packed in benzene-3% acetone with 100 mesh silica gel (Mallinckrodt), using benzene-3% acetone as an eluent. Fractions 2-6 (each 5 ml), were Ia: $\lambda_{\text{max}}^{\text{MeOH}}$ 248 and 295 m μ . Fractions 10-12 were IIa: $\lambda_{\text{max}}^{\text{MeOH}}$ 234

and 285 m μ ; ν_{max} 3430, 3370 (-NH₂), 1630, 1280 (C-N), and 750 cm⁻¹ (4 H). Fractions were IIIa: $\lambda_{\text{max}}^{\text{MeOH}}$ 240 and 288 m μ ; ν_{max} 3430, 3360 (-NH₂), 1630, 1280 (C-N), and 830 cm⁻¹ (2 H).

Effect of Oxygen or Hydroquinone on Photolysates of N-Phenylbenzylamine (Ia).—A *t*-butyl alcohol solution (30 ml) containing 0.601 g of Ia was irradiated under an oxygen atmosphere. The reaction product contained benzylideneaniline (6.0%), IIa, IIIa, IV, and Va. A mixture of 0.624 g (3.41 mmol) of Ia and 0.331 g (3.04 mmol) of hydroquinone in 1:1 isopropyl alcohol-*t*-butyl alcohol was irradiated for 20 hr. Gas chromatography of the products shows that conversion of Ia was 74.3% and the yields of IIa, IIIa, IV, and Va were 18.9, 0.9, 9.8, and 0.1%, respectively.

Photolysis of N- α -Phenethylamine (Ib).—The irradiation of Ib (0.661 g) in 1:1 isopropyl alcohol-*t*-butyl alcohol for 20 hr yielded IIb (26.0%), IIIb (8.1%), IV (9.8%), and Vb (1.9%).

Photolysis of a Mixture of N-Phenylbenzylamine (Ia) and N-(*o*-Tolyl)- α -phenethylamine (Id).—A mixture of Ia (0.308 g, 1.68 mmol) and Id (0.350 g, 1.66 mmol) in 1:1 isopropyl alcohol-*t*-butyl alcohol was irradiated for 20 hr. The reaction mixture was condensed by evaporation and analyzed by glpc. The products were identified by comparison of their retention times with corresponding authentic samples (Ib, Ic, IIa, IIb, IIIa, and IIIb) and photolysates of Ic and Id (IIc, IID, IIIC, and IIID). In all possible cross-bred products, Ib, Ic, and IIc were not observed.

Photolysis of Optically Active N- α -Phenethylamine (VI).—The photolysis was carried out with a solution of optically active N- α -phenethylamine (VI, 0.600 g, 3.04 mmol) in 30 ml of 1:1 isopropyl alcohol-*t*-butyl alcohol for 30 hr. After removal of the solvent *in vacuo*, the residual oil was fractionated by chromatography with a 15 \times 300 mm column, packed with 100 mesh silica (Mallinckrodt) in benzene; 500-g fractions were collected. Fractions 1-2 were crude Vb (26.9 mg). Fractions 4-12 were N- α -phenethylamine (VI, 242.1 mg): $\lambda_{\text{max}}^{\text{MeOH}}$ 247 m μ (log ϵ 4.09) and 296 (3.29); ν_{max} 3420 (-NH), 1315, and 1250 cm⁻¹ (C-N). Fractions 18-36 were *o*- α -phenethylamine (VII, 102.4 mg, 24.5%): mp 57.1-57.5° (lit.^{2a} mp 58.5-9.0°); $\lambda_{\text{max}}^{\text{MeOH}}$ 234 m μ (log ϵ 3.96) and 287 (3.40); ν_{max} 3450, 3360 (-NH₂), and 745 cm⁻¹ (4 H). Fractions 41-61 were *p*- α -phenethylamine (VIII, 56.8 mg, 13.6%): $\lambda_{\text{max}}^{\text{MeOH}}$ 240 m μ (log ϵ 4.64) and 289 (3.31); ν_{max} 3450, 3350 (-NH₂) and 825 cm⁻¹ (2 H). Fractions 73-78 were oil (40 mg), containing aniline. The purity of products was checked by glpc.

Optical rotatory densities of these isolated products (VI, VII, and VIII) were measured in ethyl alcohol: for N- α -phenethylamine (VI), $[\alpha]_{\text{D}}^{25} - 22.3^\circ \pm 2.1^\circ$ (*c* 0.242 g/10 cc, *l* 0.1 dm); for *o*- α -phenethylamine (VII), $[\alpha]_{\text{D}}^{25} + 3.9^\circ \pm 1.5^\circ$ (*c* 0.102 g/10 cc, *l* 0.1 dm); for *p*- α -phenethylamine (VIII), $[\alpha]_{\text{D}}^{25} - 0.9^\circ \pm 1.8^\circ$ (*c* 0.057 g/10 cc, *l* 0.1 dm).

Photolysis of Optically Active N- α -Phenethylamine (VI) in the Presence of Hydroquinone.—The photolysis was carried out with a mixture of 0.600 g (3.04 mmol) of optically active N- α -phenethylamine (VI) and 0.29 g (2.61 mmol) of hydroquinone in 30 ml of 1:1 isopropyl alcohol-*t*-butyl alcohol at room temperature for 30 hr. After similar work-up, the reaction mixture was chromatographed on a 15 \times 300 mm column, packed with 100 mesh silica gel (Mallinckrodt) in benzene; 400-g fractions were collected. Fractions 6-12 were recovered N- α -phenethylamine (VI, 100.5 mg): $\lambda_{\text{max}}^{\text{MeOH}}$ 247 m μ (log ϵ 4.07) and 2.96 (3.29); ν_{max} 3450 (-NH) and 1320 cm⁻¹ (C-N). Fractions 20-37 were *o*- α -phenethylamine (VII, 101.0 mg): $\lambda_{\text{max}}^{\text{MeOH}}$ 234 m μ (log ϵ 3.95) and 287 (3.36); ν_{max} 3460, 3360 (-NH₂), and 745 cm⁻¹ (4 H). Fractions 41-61 were *p*- α -phenethylamine (VIII, 63.05 mg): $\lambda_{\text{max}}^{\text{MeOH}}$ 240 m μ (log ϵ 4.45) and 289 (3.31); ν_{max} 3440, 3360 (-NH₂), and 825 cm⁻¹ (2 H).

Optical rotatory densities were measured in ethanol: N- α -phenethylamine (VI), $[\alpha]_{\text{D}}^{25} - 19.8^\circ \pm 1.0^\circ$ (*c* 0.101 g/10 cc, *l* 0.1 dm); *o*- α -phenethylamine (VII), $[\alpha]_{\text{D}}^{25} + 1.6^\circ \pm 0.6^\circ$ (*c* 0.101 g/10 cc, *l* 0.5 dm); *p*- α -phenethylamine (VIII), $[\alpha]_{\text{D}}^{25} - 6.0^\circ \pm 1.3^\circ$ (*c* 0.063 g/10 cc, *l* 0.5 dm).

Registry No.—Ia, 103-32-2; Ib, 23652-68-8; VI, 21232-37-1.

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