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Photochemical Rearrangement of *N*-Substituted Benzylanilines[1]

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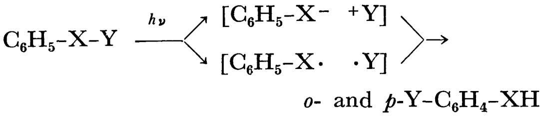
Photochemical migration of an alkyl group from nitrogen to ortho and para positions in *N*-substituted benzylanilines (I) has been studied. Quenching study suggests that the rearrangement proceeds *via* a triplet state. The rate of disappearance of *N*-(*p*-tolyl)-α-phenethylamine (III) in photolysis was found to be 3×10^7—3×10^8 sec^{-1}. Substituted benzylanilines (I) were synthesized to estimate their quantum yields of photorearrangement. A plot of the σ value for a substituent in the migrating benzyl group *vs.* logarithm of relative rate gives a positive ρ value with various quantum yields for intersystem crossing (0.1—1); the ρ value indicates that electron-withdrawing substituents in the benzyl group accelerate the rearrangement. A reaction scheme is presented.

In a previous paper,[2] it was reported that irradiation of *N*-alkylanilines with UV light gave rearranged products, *ortho*- and *para*-alkylanilines (5.5—42.5%), together with aniline (1.6—12.8%) and coupling product of alkyl radicals (0—3%). Intramolecularity of migration of the alkyl group from *N* to ortho and para positions is probable because (i) no cross-bred product was detectable, and (ii) appreciable optical activity was retained in both ortho- and para-rearranged products derived from optically active *N*-α-phenethylaniline.

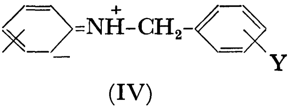
Photochemical aromatic rearrangements involving the migration of a side-chain group to the ring carbon are known with some aromatic esters,[3] amides,[4] carbonates,[5] ethers,[6] and amines.[2] So far the mechanism of rearrangement has been studied in only a few cases. As an example, it has been suggested in the photo-Fries reaction (X : O, Y : COAr) by either a molecular pathway involving ion-separated intermediate,[7-9] or a radical-pair process in which acyl-O homolysis is followed by an attack of the resulting acyl radical on the ring of phenoxy radical in a solvent cage.[10]



$$C_6H_5\text{-}X\text{-}Y \xrightarrow{h\nu} \left\{ \begin{matrix} [C_6H_5\text{-}X^- \quad {}^+Y] \\ [C_6H_5\text{-}X\cdot \quad \cdot Y] \end{matrix} \right\} \rightarrow o\text{- and } p\text{-}Y\text{-}C_6H_4\text{-}XH$$

The former molecular mechanism involving ion-separated species seems to be supported by (i) the substituent effect[8,10] with a positive ρ value for migrating benzoyl groups and a negative ρ value for aryloxy groups, (ii) acceleration by polar solvents,[9] and (iii) the quantum yield for *p*-tolyl acetate which is unaffected by a 100-fold change in solvent viscosity, in contrast with 20-fold enhancement of *p*-cresol formation.

N-Alkylanilines generally absorb 243—248 nm light to be excited to charge-separated species (IV),[2] hence electron-withdrawing groups in the migrating alkyl groups and electron-releasing groups on the anilino group of *N*-alkylanilines may accelerate the rearrangement, if the reaction proceeds *via* a zwitterionic transition state (IV).



(IV)

Since the mechanistic details of the photorearrangement of *N*-alkylanilines is unknown, we wish to report this mechanism, especially on the basis of substituent effect.

Results

Irradiation of *N*-phenylbenzylamine gave *ortho*- and *para*-benzylanilines (28.9 and 13.6%, respectively) together with aniline (5.8%) and bibenzyl (3.0%).

For elucidation of the reaction pathway, the para-position of the anilino group was shielded by a methyl group to yield ortho-rearranged product alone. A series of *N*-(*p*-tolyl)benzylamines with a substituent on the benzyl group (Ia—If) and phenylbenzylamines with a para substituent on the phenyl group (Ig—Ih) were prepared (Table 3).

The amines (Ia—If) were irradiated with ultraviolet light on a preparative scale as a solution of isopropanol–*t*-butanol (1 : 1 in vol.) (IPA–*t*-BuOH). The reaction products were separated by column chromatography, and identified and estimated by means of UV, IR, TLC and GLC techniques. The yields are summarized in Table 1. An attempt to crystallize the rearranged products failed.

In the case of the nitro compound (If), the rearranged product could not be obtained because of its slow rate of photorearrangement.

Measurement of Quantum Yields. Quantum yields for the disappearance of substrates were measured by the following method under UV light of 2537

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[1] Contribution No. 142.

[2] Y. Ogata and K. Takagi, *J. Org. Chem.*, **35**, 1642 (1970).

[3] For a review, see, for example, D. Bellus and P. Hrdlovic, *Chem. Rev.*, **67**, 599 (1967).

[4] a) D. Elad, *Tetrahedron Lett.*, **1963** 873. b) H. Shizuka and I. Tanaka, This Bulletin, **41**, 2343 (1968); **42**, 52 (1969); **42**, 909 (1969).

[5] a) C. Pac and S. Tsutsumi, *ibid.*, **37**, 1392 (1964). b) A. Davis and J. H. Golden, *J. Chem. Soc., B*, **1968**, 425.

[6] a) D. P. Kelley, J. T. Pinhey, and R. D. G. Rigby, *Aust. J. Chem.*, **22**, 977 (1969). b) D. P. Kelley, J. T. Pinhey, and R. D. G. Rigby, *Tetrahedron Lett.*, **1966**, 5953. c) Y. Ogata, K. Takagi and I. Ishino, *Tetrahedron*, **26**, 2703 (1970).

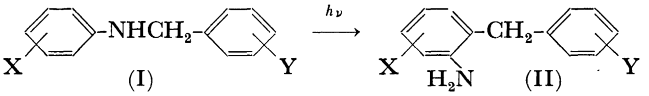
[7] M. R. Sandner and D. J. Trecker, *J. Amer. Chem. Soc.*, **89**, 5825 (1967).

[8] G. M. Coppinger and E. R. Bell, *J. Phys. Chem.*, **70**, 3479 (1966).

[9] D. A. Plank, *Tetrahedron Lett.*, **1968**, 5423.

[10] H. Kobsa, *J. Org. Chem.*, **27**, 2293 (1962).

Table 1. Photochemical rearrangement of substituted N-benzylanilines[a]



Photolysate	X	Y	Conv. (%)	Yield (%)[b]	Irrad. time (hr)
IIa	p-Me	p-Me	34.7	24.9	51
IIc	p-Me	H	56	24	40
IId	p-Me	p-Cl	76	12	31
IIe	p-Me	p-CN	56	31	51

a) In a IPA$-t$-BuOH (*ca.* 0.1 M). The mixtures were condensed by evaporation and chromatographed on a 300×20 mm column of SiO$_2$. Isomers were confirmed by IR ($-$NH$_2$), UV, TLC, and GLPC.

b) Based on the consumed substrates.

Å with a low pressure mercury lamp (Halos POL 30). Light intensities were measured with a potassium ferrioxalate solution. Disappearance of secondary amines was potentiometrically determined by Siggia's method.[11]

The reaction was interrupted when the conversion was less than *ca.* 20% to minimize the absorption of the UV light by photoproducts. The quantum yields of the p-toluidine formation were determined by GLC. The results are summarized in Table 2.

Table 2. Quantum yields for the disappearance of substituted N-benzylanilines and formation of p-toluidine

Substituted N-benzylaniline	X	Y	Quantum yield (ϕ)	
			Disappearance of starting material	Toluidine formation[b]
Ia	p-Me	p-Me	0.16±0.01	0.06±0.01
Ib	p-Me	m-Me	0.15±0.01	0.05±0.01
Ic	p-Me	H	0.20±0.02	0.08±0.03
Id	p-Me	p-Cl	0.23±0.03	—
Ie	p-Me	p-CN	0.27±0.03	trace
If	p-Me	p-NO$_2$	0.13±0.02	—
Ig	p-MeO	H	0.22±0.01	—[a]
Ih	p-Cl	H	—[a]	—[a]

a) Not determined.

b) Decomposition product.

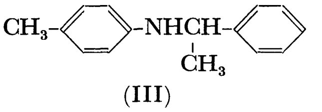
In the case of amines with an electron-withdrawing group, especially in Ih with para-chloro group in the anilino group, a decrease of amine basicity made potentiometric determination of quantum yield difficult. Table 2 lists average quantum yields calculated from at least three observed values. The difference between these quantum yields is regarded as significant beyond experimental error. The potentiometry was checked to give reliable data of less than 10% error in comparison with GLC technique.

Reaction Multiplicity. In a preliminary experiment, a heavy atom effect was observed, *i.e.*, the photorearrangement of N-(p-methylbenzyl)aniline was accelerated in n-propyl chloride compared with that in n-hexane. The result seems to indicate the intermediacy of a triplet state.[12] The reaction multiplicity was further confirmed by quenching experiments. Solutions of 0.02—0.03 M N-(p-tolyl)-α-phenethylamine in IPA-t-BuOH containing a quencher, naphthalene, were irradiated on a merry-go-round apparatus with 2537 Å light. A plot of reciprocal of quantum yield *vs.* quencher concentration lies on a good straight line. The disappearance of substrate and the formation of the rearranged product were measured by GLC.

In quenching by naphthalene, self absorption by the quencher may affect the intensity of incident light. As an example, the ratio of the light quanta absorbed by naphthalene to those by Ia was calculated to be more than 20% in the presence of two equivalent amounts of naphthalene. A singlet state as well as a triplet state may be quenched. Quenching by piperylene was also examined. The Sterm-Volmer plots obtained with piperylene is shown in Fig. 1, in which a fairly good linearity is observed. Piperylene was confirmed to be transparent at least at a wavelength longer than 250 nm, although it exhibits an absorption maximum at 232 nm in methanol. In the measurement of fluorescence intensities of Ia with various amounts of piperylene, neither fluorescence intensity nor the maximum at 370 nm varies with the change of 0—4.5 equivalents amount of piperylene, which implies that piperylene does not quench the singlet of Ia at all, since the Stern-Volmer plot of Fig. 1 is obtained within a range of 3 equivalents amount of piperylene.

The results suggest that the rearrangement occurs *via* a triplet state. The energy transfer from the excited substrate to the quencher would be allowed, since the triplet energies of 61 kcal/mol (naphthalene) and 59 kcal/mol (piperylene) are probably lower than that of substrate, which is expected to be *ca.* 70 kcal/mol from those of aniline (77 kcal/mol), diphenylamine (72 kcal/mol) and triphenylamine (70 kcal/mol).

Measurement of the Rate of Photolysis of III. Aqueous monochloroacetic acid is easily hydrolyzed to give glycolic acid and chloride ion by irradiation of 2537 Å light. The quantum yield for the hydrolysis of the acid (0.5 M) has been determined to be 0.351 at 28°C.[13] The solution was employed as a chemical actinometer, as it is convenient to measure the light intensities of 2537 Å in diffused light. The amount of 0.02 M N-(p-tolyl)-α-phenethylamine(III) in IPA-t-BuOH containing an appropriate amount of piperylene was irradiated by 2537 Å light at 28°C with a merry-go-round apparatus.



(III)

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[11] S. Siggia, J. G. Hanna, and I. R. Kervenski, *Anal. Chem.*, **20**, 1295 (1950).

[12] S. P. McGlynn, M. J. Reynolds, G. W. Daigre, and N. D. Christobouleos, *J. Phys. Chem.*, **66**, 2499 (1962); S. P. McGlynn, F. J. Smith, and G. Cilento, *Photochem. Photobiol.*, **3**, 269 (1964).

[13] a) R. N. Smith, P. A. Leighton, and W. G. Leighton, *J. Amer. Chem. Soc.*, **61**, 2299 (1939). b) L. B. Thomas, *ibid.*, **62**, 1879 (1940).

The conversion of substrate was determined by GLC using acenaphthene as an internal standard. The quantum yield for the disappearance of substrate was calculated to be 0.10 in the absence of a quencher. The Stern-Volmer plots (*cf.* Eq. (2)) obtained from reciprocals of the quantum yields ($1/\phi$) against the piperylene concentration ([Q]) gave a straight line, with a slope of 90 as shown in Fig. 1.

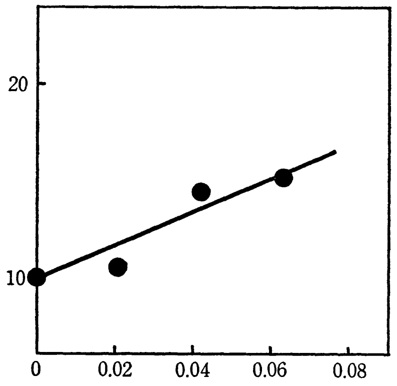


Fig. 1. Stern-Volmer plot of the disappearance of 0.02 M *N*-(*p*-toly)-α-phenethylamine (III).

The quenching rate was estimated by the following Debye equation.

$$k_q = 8\boldsymbol{R}T/3000\eta \qquad (1)$$

The rate constant k_q was $2.4\times10^9\ \text{M}^{-1}\cdot\text{sec}^{-1}$, since the viscosity of IPA–*t*-BuOH, was found to be 0.0196 poise at 28°C. In the following Stern-Volmer equation, where k_d and k_r are rate constants for deactivation and reaction, respectively, [Q], the concentration of a quencher, and $f(=\phi_{\text{isc}})$, the quantum yield for intersystem crossing from excited singlet state to excited triplet state (Eq. (5)),

$$1/\phi = \{(k_d+k_r)/f\cdot k_r\} + \{k_q\cdot[\text{Q}]/f\cdot k_r\}, \qquad (2)$$

the slope of the plot of $1/\phi$ *vs.* [Q] gave

$$k_q/f\cdot k_r = 90 \qquad (3)$$

Assuming that the quenching rate is equal to the diffusion-controlled rate, we have $f\cdot k_r = 2.7\times10^7\ \text{sec}^{-1}$. The rate constant for the rearrangement was calculated to be 2.7×10^7—$2.7\times10^8\ \text{sec}^{-1}$ because of $0.1 < f < 1$.

Discussion

The photochemical primary and secondary processes of the reaction can be expressed by means of Eqs. (4)—(10).

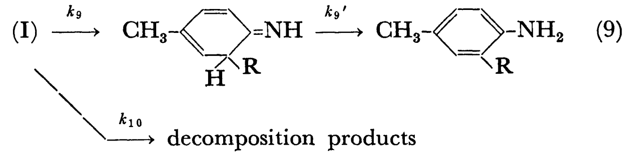
$$\underset{(\text{A}^0)}{p\text{-CH}_3\text{-C}_6\text{H}_4\text{-NHR}} \xrightarrow{h\nu} \text{A}^1 \qquad (4)$$

$$\text{A}^1 \xrightarrow{k_{st}} \text{A}^3 \qquad (5)$$

$$\text{A}^3 \xrightarrow{k_d} \text{A}^0 \qquad (6)$$

$$\text{A}^3 \xrightarrow{k_r} \underset{(\text{I})}{[p\text{-CH}_3\text{C}_6\text{H}_4\text{-NH}\cdots\cdots\text{R}]} \qquad (7)$$

$$\text{A}^3 + \text{Q} \xrightarrow{k_q} \text{A}^0 + \text{Q}^3 \qquad (8)$$



decomposition products

(*p*-toluidine and bialkyl) (10)

These equations give the quantum yield (ϕ) for the disappearance of substrate as

$$\phi = f\cdot k_r/(k_d + k_r + k_q[\text{Q}]) \qquad (11)$$

From this equation, we obtain the following equation, since no quencher is added to the mixture, *i.e.*, [Q]=0.

$$\frac{1/\phi_{\text{H}} - 1/f_{\text{H}}}{1/\phi_{\text{X}} - 1/f_{\text{X}}} = \frac{f_{\text{X}}\cdot k_{r\text{X}}\cdot k_{d\text{H}}}{f_{\text{H}}\cdot k_{r\text{H}}\cdot k_{d\text{X}}} \qquad (12)$$

Here, subscript X and H denote *N*-(*p*-tolyl)benzylamine substituted and unsubstituted in the benzyl ring, respectively; subscripts k_r and k_d denote the rate constants for Eqs. (6) and (7), respectively.

In general, the observed quantum yields for substituted *N*-(*p*-tolyl)benzylamines (I) decrease with the increase of electron-donative ability of the substituent, *e.g.*, from 0.27 in Ie (*p*-CN) to 0.16 in Ia (*p*-Me). The approximate linearity of the plot of log ϕ *vs.* Hammett σ was observed, in which a trend of an increase of the quantum yield with the increase of σ is obvious.

Since little information concerning f values is available at present, the following approximation was deduced to see a correlation between the σ value and the relative rate constant $k_{r\text{X}}/k_{r\text{H}}$, *i.e.* the approximate independence of f and k_d on substituents.

Firstly, as suggested by Lamola and Hammond,[14a] quantum yield f for intersystem crossing would depend little on substituent X, *i.e.*, $f_{\text{H}} \sim f_{\text{X}} \sim f$. They suggested that the same factors influence the rates of radiationless transitions ($S^1 \rightarrow S^0$) and intersystem crossing ($S^1 \rightarrow T^1$) in studying the substituent effect of substituted naphthalene on their quantum yields for f values. This means that a substituent hardly affects the efficiency of intersystem crossing.

Secondly, it can be assumed that the deactivation process (corresponding to $k_{d\text{X}}$) from a π–π^* excited state (as well as n–π^*) is hardly affected by substituent X. The approximate constancy of $k_{d\text{X}}$, but not $k_{r\text{X}}$, is often reported.[14b–f] Zimmerman[14c,d] estimated that the decay rate constant k_d remains nearly constant in the photorearrangement of 4,4′-diarylcyclohexanone, while k_r varies over *ca.* 100-fold. Mallory[14e] and Jungmann[14f] reported the substituent effect on the photocyclization of stilbenes to the corresponding phenanthrenes *via* a π–π^* excited state, in which a nice Hammett correlation with the correlation factor of 0.9996 between $k_{r\text{X}}/k_{r\text{H}}$ and σ is observed assuming the decay

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[14] a) A. A. Lamola and G. S. Hammond, *J. Phys. Chem.*, **43**, 2129 (1965). b) N. C. Yang and R. L. Dusenbery, *J. Amer. Chem. Soc.*, **90**, 5899 (1968). c) H. E. Zimmerman and W. R. Elser, *ibid.*, **91**, 887 (1969). d) H. E. Zimmerman and N. Lewin, *ibid.*, **91**, 879 (1969). e) F. B. Mallory, J. T. Gorden, and C. S. Wood, *ibid.*, **85**, 828 (1963). f) H. Jungmann, H. Grünsten, and D. Schlte-Frohlinde, *Chem. Ber.*, **101**, 2690 (1968).

rate constant k_{dX} remains constant. The results seem to support the assumption that k_{dX} is approximately constant.

The substituents on the migrating benzyl group are expected to have less effect on the decay process of the excited energy on the aniline ring moiety of the substrate, if the excitation energy related to the 2537 Å light absorption at the latter moiety is localized on the aniline ring.[15]

From the above approximation, we have tentatively assumed that k_{dX} and f_X are independent of X for Ia—If studied. Hence, $(f_X/f_H)(k_{dH}/k_{dX})$ may be approximately constant, and Eq. (12) can be simplified to

$$\frac{1/\phi_H-1/f}{1/\phi_X-1/f}=\alpha\frac{k_{rX}}{k_{rH}} \qquad (13)$$

where $\alpha=f_X\cdot k_{dH}/(f_H\cdot k_{dX})$. The Hammett equation is then applicable as in Eq. 14 which is shown in Fig. 2 based on the data on Table 2.

$$\log\left(\frac{1/\phi_H-1/f}{1/\phi_X-1/f}\right)=\sigma\rho+\text{const.} \qquad (14)$$

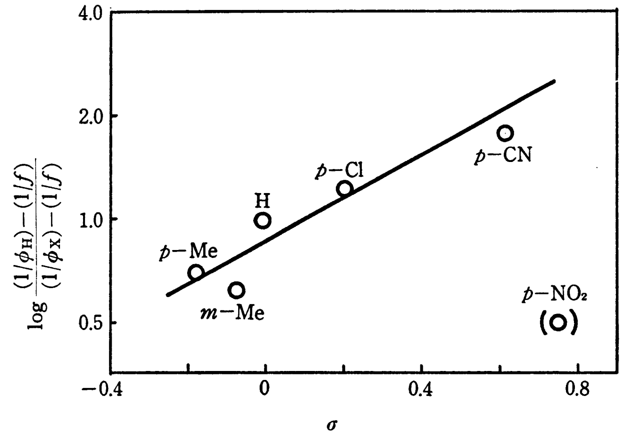


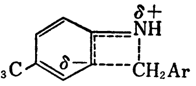
Fig. 2. Relationship between $\log\frac{(1/\phi_H)-(1/f)}{(1/\phi_X)-(1/f)}$ and σ with quantum yields for intersystem crossing (f) of 0.5.

The nitro compound was excluded, since its unusual behavior would be due to the deactivation of excited compound by the reduction of the nitro group to nitroso[16] and/or amino groups.[17]

The σ values used for the plot were quoted from Jaffe's review.[18] A positive ρ value was obtained from Fig. 2 with values of f 0.1—1. A plot of Eq. (14) gave a better correlation than that of $\log\phi$ *vs.* σ value. This also supports the above approximation that k_{dX} is less affected by substituent. A linear Hammett plot has been presented in the photo-Fries reaction,[8,10] which seems to suggest the validity of the Hammett equation for some photoreactions.

The electron density on the anilino nitrogen atom is delocalized into the ring in an excited state of *N*-alkylaniline (*cf.* IV). In the case of ionic mechanism, the requirement for the rearrangement is the electron defficiency at benzyl carbon and the electron richness at ortho position of the anilino ring, thus a positive ρ value for the migrating group can be expected. This ionic scheme, however, cannot explain the by-product, bialkyl. It is natural that the rearrangement almost certainly proceeds *via* a radical process, although the possibility of an ionic rearrangement cannot completely be discarded.

Our previous view that the optical activity is retained in the photorearrangement of optically active *N*-α-phenethylaniline excludes the possibility of the intermediacy of free benzyl radical which should be nearly planar in the migrating transition state. Thus either a bridged intermediate (V), or a radical-pair resulting from the scission of nitrogen-benzyl bond, which can very rapidly recombine in a solvent cage,[10] is conceivable in the transition state.



(V)

The positive ρ value can be explained by either reaction scheme. In the bridged scheme, the activated complex V should have more complete benzyl-ortho carbon bond and less complete benzyl-amino nitrogen bond, hence an electron-withdrawing group in the benzyl group can accelerate the rearrangement, because the rate seems to be determined by the electrophilic attack of the benzyl group but not by the benzyl-nitrogen bond fission.

In another mechanism of the homolytic scission in a solvent cage, the positive ρ value can be explained as follows. The rate-determining step for the homolytic rearrangement may be the coupling of benzyl radical with the anilino radical to give products, since the C–N fission step should be rapid in view of the analogous photo-rearrangement of *p*-substituted acetanilides which have high relative ratios ($\phi_B/\phi_F\sim3$) of quantum yields for coupling of $CH_3CO\cdot$ and $Ph\text{-}NH\cdot$ to give starting materials (ϕ_B) compared to those of the forward reactions (ϕ_F).[4b] The observed ρ value suggests a higher contribution of substituent effect on the electrophilic nature of benzyl radical for an attack on the benzene ring. Although the substituent effect of benzyl radical attack is unavailable, reaction rates for phenylation of toluene by substituted phenyl radicals have been reported to vary with substituents in the order: p-$NO_2>p$-$Cl>H>p$-Me.[19] This means that the phenylation of toluene has a positive ρ value. Also the effect of substituent in the aryloxy ring in photo-Fries reaction is known to have a positive ρ value.[8,10]

On the other hand, the effect of substituent in anilino group on the present rearrangement is obscure on account of the small number of substituents and the difficulty in analysis. Further, the problem is complicated by the fact that a substituent para to the amino group is also meta to the attacking site. Observed

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[15] Suggested by the referee.

[16] S. H. Hasting and F. A. Matsen, *J. Amer. Chem. Soc.*, **70**, 3514 (1948).

[17] R. Hurley and A. C. Testa, *ibid.*, **88**, 4330 (1966).

[18] H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

[19] W. A. Pryor, "Free Radicals," McGraw-Hill Co., New York, N. Y. (1960), p. 262.

quantum yields are 0.20 (p-Me) and 0.22 (p-MeO), which are comparable to those observed with the substituents in benzyl groups.

Experimental

All mp and bp are uncorrected. IR spectra were measured by the method of liquid film using a Perkin-Elmer grating infrared spectrophotometer Model 337. UV spectra were measured with a Shimadzu UV spectrophotometer Model SV-50 A or a Hitachi spectrophotometer Model 124. GLC analysis was carried out by means of a Yanagimoto gas chromatograph with FID, Model GCG-550 F, employing a 1.7 m×2.5 mm column packed with PEG 20 M (2.5wt%) on Chamelite CS of 80—100 mesh using N_2 as a carrier gas at 160—250°C. Fluorescence spectra were measured at room temperature with a Hitachi fluorescence spectrophotometer, Model MPF-2A.

Preparation of Substituted Benzylanilines (I). Benzylanilines were prepared by the reaction of p-substituted anilines with substituted benzyl chlorides (or bromides) in an aqueous benzene solution containing $NaHCO_3$.[2] The products were purified by vacuum distillation, except for p-cyano (Ie) and p-nitro compounds (If) which solidified on distillation of starting materials and was purified by recrystallization from petroleum ether. The starting materials are listed in Table 3. All these amines were chromatographed for complete removal of unreacted toluidine before use.

Preparation of N*-(p-Tolyl)-α-phenethylamine (III).* N-(p-Tolyl)-α-phenethylamine(III) was prepared by the reaction of p-toluidine with α-chloroethylbenzene, mp 68.5—69°C (from petroleum ether), bp 130—133°C/2.5 mmHg, λ_{max}^{MeOH} (nm) (log ε), 248(4.10) and 302(3.27).

Isolation of Rearranged Products. On irradiation of N-substituted benzyl(p-tolyl)amines in a preparative scale, rearranged products were isolated.

All experiments were carried out in a cylindrical quartz vessel (20×150 mm) under N_2. A Halos high 300 W Hg lamp with a water cooling quartz jacket was used as a light source. Isolated products were identified and estimated by IR, UV, TLC, and GLC.

(2′-Amino-4′-methylphenyl)-4-methylphenylmethane (IIa). A solution of Ia (0.7 g) in i-PrOH-t-BuOH (30 ml) was irradiated in a quartz vessel for 51 hr. The condensed reaction mixture was chromatographed on a 15×300 mm column, slurry packed in benzene with 80—100 mesh silica gel, using benzene (600 g) and benzene- 3% acetone (100 g) as eluents. Fractions 4—9 was Ia (451 mg), fractions 21—41 was IIa (pale yellow oil, 63.4 mg, 24.9%), λ_{max}^{MeOH} (nm), 238, 292; ν_{max} (cm^{-1}), 3430, 3350, and fraction 85 was p-toluidine (62 mg).

(2′-Amino-4′-methylphenyl)phenylmethane (IIc). A solution of Ic (0.7 g) in i-PrOH-t-BuOH (30 ml) was irradiated for 40 hr. Column chromatography gave recovered starting material (Ic, 350 mg) and a rearranged solid product (IIc, 107 mg, 24%), λ_{max}^{MeOH} (nm), 237, 292; ν_{max} (cm^{-1}), 3430, 3350 (primary amine).

(2′-Amino-4′-methylphenyl)-4-chlorophenylmethane (IId). A solution of Id (0.7 g) in i-PrOH-t-BuOH (30 ml) was irradiated for 31 hr. In a similar manner, recovered Id (168 mg) and a rearranged liquid product (IId, 64 mg, 12%) were isolated, λ_{max}^{MeOH} (nm), 240 (sh), 294; ν_{max} (cm^{-1}), 3420, 3350 (primary amine), 1090 (C–Cl).

(2′-Amino-4′-methylphenyl)4-cyanophenylmethane (IIe). A solution of Ie (1.795 g) in ethanol (120 ml) in a quartz vessel (35×170 mm) was irradiated for 51 hr at room temperature. Rearranged product IIe (246 mg, 31%) was separated from the reaction mixture by column chromatography, λ_{max}^{MeOH} (nm), 235, 295; ν_{max} (cm^{-1}), 3430, 3350 (primary amine), 2200 (C–N). Rearranged products, except IIc, could not be crystallized even by keeping in an ice-box.

2-Phenethyl-4-methylaniline (IV). A solution of III (0.82 g) in methanol (30 ml) was irradiated in a quartz vessel for 25 hr. The condensed reaction mixture was similarly treated to yield the rearranged product (IV, 155 mg, 22%), ν_{max} (cm^{-1}), 3430 and 3350 (primary amine).

Measurement of Quantum Yield. Quantum yields were determined by method A or B. Method A affords the quantum yield for photolysis of N-benzylainlines, and method B

TABLE 3. PHYSICAL PROPERTIES OF SUBSTITUTED N-BENZYLANILINES[a]

	X	Y	bp (°C/mmHg)	mp (°C)	λ_{max} (log ε) in MeOH	
Ia	p-Me	p-Me	130—137/0.5	54.5—55.0 (61—61)[19]	249 (4.18)	301 (3.26)
Ib[b]	p-Me	m-Me	137—140/1—2	liq.	246 (4.10)	302 (3.27)
Ic	p-Me	H	130—137/0.5 (312—313/760)[20]	liq.	249 (4.13)	302 (3.23)
Id	p-Me	p-Cl	140—147/0.5	46.5—47.0 (47—48)[20]	248 (4.19)	301 (3.31)
Ie[b]	p-Me	p-CN	—	90—92	241 (4.37)	300 (3.37)
If	p-Me	p-NO_2	—	68—70 (68)[21]	250 (4.26)	
Ig	p-MeO	H	160—170/1—2 (236—238/32)[22]	47—49 (52)[22]	249 (4.18)	312 (3.35)
Ih	p-Cl	H	138—150/1	42—43.5 (45)[23]	257 (4.30)	308 (3.34)

a) All materials were purified by column chromatography. b) New compound.

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was used for quenching studies to measure the rate of photolysis of *N*-(*p*-tolyl)-α-phenethylamine (III).

Method A. A spiral type low pressure Hg lamp (Halos POL 30) was employed as a light source of 2537 Å. The light intensity incident on the sample was measured by a potassium ferrioxalate solution as a chemical actinometer. The long-size quartz cell (50×24 mm) for UV spectrophotometer was used as a reaction vessel with flat faces perpendicular to light beams.

About 23 m*l* of a *ca.* 0.04 M amine solution in *i*-PrOH-*t*-BuOH was photolyzed until 20% conversion was attained.

After irradiation, the reaction mixture was diluted to 25.0 m*l* with isopropanol. The amount of photolyzed amine was determined by Siggia's method.[11]

An aliquot (10 m*l*) of the above product solution, after dilution with ethylene glycol (10 m*l*), was potentiometrically titrated with 0.1 N HCl in ethylene glycol-isopropanol.

Neutralization point was determined by plotting the apparent pH against volume of the acid solution to give the total amount of secondary plus primary amines.

Another aliquot (10 m*l*) of the solution was added with ethylene glycol (10 m*l*), and titrated similarly with acid to estimate the amount of the secondary amine after 30 min. mixing excess salicylaldehyde (*ca.* 0.3 m*l*). The amount of photolyzed amine was calculated as a difference (total amine)−(secondary amine), within ±10% experimental error. For example, an *i*-PrOH-*t*-BuOH solution of Ia (1.00×10^{-3} mol) was irradiated by 2537 Å for 10 hr, and then diluted to 25.0 m*l*. An aliquot (10 m*l*) of the diluted solution was potentiometrically analyzed for unreacted secondary amine to be 0.65×10^{-3} mol and the other aliquot (5 m*l*) for the unreacted amine to be 0.59×10^{-3} mol by the method of GLC analysis. Both analytical methods exhibit relative experimental errors below 10%.

Method B. A cylindrical low pressure Hg lamp (Halos HIL 30) was employed as a 2537 Å light source. Irradiation was carried out under diffused light on a turn table which rotates around the light source. Five cylindrical quartz vessels (200×8 mm) were used for the reaction. The incident light intensities were measured on the basis of the known quantum yield (0.351 at 28°C) for photochemical hydrolysis of 0.5 M aqueous monochloroacetic acid by 2537 Å irradiation.[13] The chloride ion produced from the acid was measured by means of back-titration of excess silver nitrate by standard ammonium thiocyanate. An aqueous solution of the acid was photolyzed for 3 hr to yield *ca.* 1.0×10^{-4} mol of chloride ion.

For the quenching studies, a solution of 0.02—0.03 M *N*-(*p*-tolyl)-α-phenethylamine in *i*-PrOH-*t*-BuOH (10 m*l*) containing an appropriate amount of the quencher (0—0.15 M in naphthalene, 0—0.06 M in piperylene) was used.

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