Mechanism of the Oxidation of *N*-Benzylanilines to Benzylideneanilines by Halogen or Hypohalite in Alkaline Methanol

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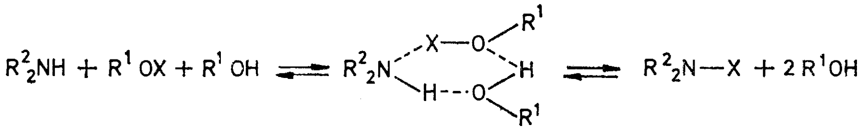
The mechanism of the oxidation of *N*-benzylanilines to benzylideneanilines with iodine, chlorine, bromine, or t-butyl hypochlorite in alkaline methanol has been studied by examination of the kinetics and by isolation of intermediates. A kinetic study is possible only with iodine because of the rapid consumption of chlorine, bromine, and t-butyl hypochlorite in organic solvents. The rate is changed by the amount of added iodine, *i.e.*, $v = k[\mathrm{PhCH_2NHPh}][\mathrm{MeOI}]$ for a large excess of alkali over iodine and $v = k'[\mathrm{PhCH_2NHPh}]([\mathrm{MeO^-}]_t/[\mathrm{I_2}]_t - 1)$ for a small excess of alkali over iodine, where subscript t refers to the total concentration of reagent. The effect of ring substituents on the rate at 25° in the presence of a large excess of alkali gives a ρ value of $-1{\cdot}15$ for substituents on the aniline ring and $+0{\cdot}38$ for substituents on the benzyl ring. *N*-Benzylaniline reacts with molecular chlorine or bromine in the absence of a base to give *N*-benzyl-*N*-halogenoanilinium halide, which gives *N*-benzyl-*o*- and -*p*-halogenoanilines but no benzylideneaniline upon treatment with alkaline methanol. A mechanism is postulated, which involves a rate-determining attack of hypohalite on both the amine nitrogen atom and a benzyl proton *via* a cyclic transition state, giving a zwitterion; this zwitterion rearranges to *N*-α-halogenobenzylaniline, which is dehydrohalogenated to benzylideneaniline.

THERE have been a number of studies on the oxidation of amines with halogenating agents,[1-3] but no detailed mechanism has been elucidated. Dunstan *et al.*[1a] postulated the intervention of an enamine in the reaction of $\mathrm{R^1CH_2CH_2NR^2_2}$ with *N*-bromosuccinimide giving $\mathrm{R^1CH_2CHO}$ and $\mathrm{R^2_2NH}$, while Horner *et al.*[1b] suggested the intermediacy of α-halogenoalkylamines for this reaction.

The reaction of primary and secondary amines with hypohalites gives *N*-halogenoamines [reaction (1)].[2] On the other hand, secondary amines bearing an α-hydrogen atom react with basic hypohalites to yield imines.[3] For example, *N*-benzylanilines react with hypohalites in alkaline solvents to give benzylideneanilines [reaction (2)]. Bachmann *et al.*[3a] suggested a mechanism for this reaction involving the initial formation of *N*-halogenoamines without convincing evidence. However, there may be another mechanism which involves the intermediate formation of α-halogenoalkylamine.

This paper summarises our kinetic results and discusses the mechanism for the oxidation of secondary amines bearing an α-hydrogen atom (*N*-benzylanilines) with hypohalites in basic methanol to give imines (benzylideneanilines).


(1)

$$\mathrm{Ar^1CH_2NHAr^2 + ROX + RO^- \longrightarrow Ar^1CH{=}NAr^2 + 2\,ROH + X^-} \qquad (2)$$

EXPERIMENTAL

Materials.—*N*-Benzylanilines were prepared by the treatment of benzyl chlorides with anilines in the presence

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[1] (*a*) S. Dunstan and H. B. Henbest, *J. Chem. Soc.*, 1957, 4905; (*b*) L. Horner, E. Winkeln, K. H. Knapp, and W. Ludwig, *Chem. Ber.*, 1959, **92**, 288; (*c*) M. Okawara, H. Sato, and E. Imoto, *Kogyo Kagaku Zasshi*, 1957, **60**, 1146; (*d*) P. F. Kruse, K. L. Grist, jun., and T. A. McCoy, *Analyt. Chem.*, 1954, **26**, 1319; (*e*) D. G. Lee and R. Srinivasan, *Canad. J. Chem.*, 1973, **51**, 2546.

[2] (*a*) I. Weil and J. C. Morris, *J. Amer. Chem. Soc.*, 1949, **71**, 1664; (*b*) T. Higuchi, U.S. Dept. Commerce Office Technical Rev. AD, 1962, No. 412,343, p. 7 (*Chem. Abs.*, 1964, **60**, 9115g); (*c*) J. C. Morris, Principles Appl. Water Chem., Proc. 4th Rudolf Research Conference, Rutgers State Univ., 1965, p. 23 (*Chem. Abs.*, 1968, **68**, 43,594t).

[3] (*a*) W. E. Bachmann, M. P. Cava, and A. S. Dreiding, *J. Amer. Chem. Soc.*, 1954, **76**, 5554; (*b*) L. Hellermann and A. G. Sanders, *ibid.*, 1927, **49**, 1742; (*c*) H. Lettre and L. Knof, *Chem. Ber.*, 1960, **93**, 2860; (*d*) A. Brossi, F. Schenker, and W. Leimgruber, *Helv. Chim. Acta*, 1964, **47**, 2089.

of aqueous Na_2CO_3 at 95—100°.[4] They were distilled or recrystallized from n-hexane if solid. The substituted *N*-benzylanilines, $YC_6H_4CH_2NHC_6H_4Z$, gave b.p.s, m.p.s, and g.l.c. retention times (R_t) for a DEGS column as follows: unsubstituted, b.p. 163—165° at 5 mmHg, m.p. 36·0—36·5°, R_t 13·6 min (9·7 min for SE 30); Y = *p*-Cl, Z = H, b.p. 165—166° at 2·5 mmHg, 22·5 min; Y = *m*-Cl, Z = H, b.p. 155—157° at 3·0 mmHg, 20·2 min; Y = *p*-Me, Z = H, m.p. 45·0—45·5°, 14·8 min; Y = H, Z = *p*-Cl, b.p. 132—135° at 2·5 mmHg, m.p. 36·0—37·0°, 21·4 min (12·0 min for SE 30); Y = H, Z = *m*-Cl, b.p. 145—146° at 2·7 mmHg, 19·2 min; Y = H, Z = *p*-Me, b.p. 145—148° at 4·5 mmHg, 14·8 min; Y = H, Z = *p*-MeO, b.p. 150—152° at 3·5 mmHg, m.p. 43—44°, 31·3 min (14·7 min for SE 30). A Hitachi K 53 gas chromatograph with a flame ionization detector was used with a 1·5 m × 3 mm column packed with DEGS (13%) on Chromosorb W at 100—220° (increasing by 10° min^{-1}), or with a 2·0 m × 3 mm column packed with SE 30 (3%) on Chromosorb W at 100—280° (increasing by 10° min^{-1}) with N_2 as a carrier gas in a flow rate of 70 ml min^{-1}. Methanol was dried (CaO) and distilled, b.p. 64·5—64·7°. Iodine (63·5 g) was added to a methanolic solution (250 ml) of 1·0M-sodium methoxide and diluted to 500 ml by addition of pure methanol giving a 0·5M solution.

Products.—*N*-Benzylanilines in methanol containing an excess of sodium methoxide over hypohalite reacted with iodine, chlorine, bromine, or t-butyl hypochlorite at 25° to give benzylideneanilines in yields >95%. However, when 2M-sodium methoxide (10 ml) was added to a mixture of *N*-benzylaniline (1·8 g) and t-butyl hypochlorite (1·0 g) in ether (10 ml), the products were benzylideneaniline (52%) and *o*- and *p*-chloro-*N*-benzylanilines (47%). The use of calcium hypochlorite instead of t-butyl hypochlorite gave similar results. The products were identified by g.l.c. on a column packed with DEGS (13%) and SE 30 (3%). *N*-Benzyl-*N*-chloroanilinium chloride, m.p. 160—165°, $\nu_{max.}$ 2700, 2550, 2400, 1590, 775, and 690 cm^{-1}, prepared by the treatment of *N*-benzylaniline with molecular chlorine in ether, gives only *o*- and *p*-chloro-*N*-benzylanilines (45—53%), *N*-benzylaniline being recovered (47—55%) on addition of methanolic sodium methoxide. The use of molecular bromine gave the same results.

On the other hand, no *N*-benzyl-*N*-iodoanilinium iodide was precipitated on similar treatment of *N*-benzylaniline with iodine in ether. The addition of sodium methoxide to an ethereal solution of *N*-benzylaniline and iodine yielded only benzylideneaniline. But in the absence of base, *N*-benzylaniline reacts with iodine at 64° to give *N*-benzyl-*p*-methoxyaniline. The products were listed in Table 1.

TABLE 1

Products in the reaction of *N*-benzylaniline (0·01M) with iodine (0·02M) in methanol

Condition of reaction				Composition of product (%)	
$[MeO^-]_t$/M	Temp. (°C)	*t*/h	Conversion (%)	(Vc) [a]	(IVb)
	25	10	0		
	64	10	42	42	58
0·01	64	10	97	7	93
0·20	25	3	96	0	100

[a] This value contains the amount of *p*-methoxybenzylideneaniline produced from (Vc).

Kinetics.—The rate of reaction of *N*-benzylanilines (2·5—3·2 × 10^{-3}M) in methanol with a large excess of iodine (7·5—200 × 10^{-3}M) and sodium methoxide (100—600 × 10^{-3}M), where the total amount of sodium methoxide was always in excess of that of iodine, was measured by means of g.l.c. analysis of the remaining *N*-benzylaniline. The rate could not be measured by following changes in the iodine or hypohalite concentrations which varied by spontaneous decomposition or by reaction with methanol, although these changes may be small.

The kinetic procedure was as follows. A mixture of the appropriate amounts of methanolic sodium methoxide, *N*-benzylaniline, and biphenyl (as an internal standard) was thermostatted at 25·0°. The reaction was started by addition of a methanolic solution of 0·5M-iodine. At appropriate intervals, aliquot portions were taken out and extracted with chloroform. The chloroform extract was washed with aqueous $Na_2S_2O_3$ and the solvent was evaporated. The *N*-benzylaniline content was measured by g.l.c. with a column packed with DEGS (13%). A plot of log($[PhCH_2NHPh]_0/[PhCH_2NHPh]$) against time gives a straight line up to 80—90% conversion.

The rate of the reaction of *N*-benzylanilines with chlorine, bromine, or t-butyl hypochlorite could not be measured because of the very rapid reaction of methanol with these reagents.

RESULTS

Rate Law.—The reaction of *N*-benzylaniline with a mixture of iodine and sodium methoxide is irreversible and the reaction rate in methanol was measured by means of g.l.c. analysis of the benzylaniline at 25°, where the total amount of sodium methoxide was always in excess over that of iodine ($[RO^-]_t > [I_2]_t$). The pseudo-first-order rate constants (k_{obs} in the rate equation $v = k_{obs}[PhCH_2NHPh]$) are satisfactorily constant up to 80—90% conversion, and are listed in Table 2. Plots of k_{obs} *vs.* $[I_2]_t$ (total concentration of added iodine) are shown in Figure 1.

TABLE 2

Pseudo-first-order rate constants for the reaction of *N*-benzylaniline with iodine in methanolic sodium methoxide at 25°

$10^3[NaOMe]_t$/M	$10^3[I_2]_t$/M	$10^{-3}k_{obs}/s^{-1}$ [a]
500	50·0	1·53
500	75·0	2·14
500	100	2·53
500	125	3·36
500	150	0·512
500	175	0·290
500	200	0·082
500	200	0·123
600	50·0	1·81
400	50·0	1·44
300	50·0	1·47
200	50·0	1·37
200	25·0	0·600
200	37·5	1·29
200	62·5	0·772
200	75·0	0·448
200	125	0·059
100	7·5	0·223
100	12·5	0·413
100	18·8	0·550
100	25·0	0·602
100	37·5	0·461
100	50·0	0·280
100	75·0	0·072

[a] k_{obs} Was obtained from the slope of plot of log ($[PhCH_2NHPh]_0/[PhCH_2NHPh]$) against time.

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[4] F. G. Willson and T. S. Wheeler, *Org. Synth.*, 1941, Coll. Vol. I, p. 102.

In the presence of a large excess of alkali over iodine, where iodine is almost completely converted into hypohalite, the rate is proportional to the amount of added iodine, *i.e.*, methyl hypoiodite [equation (3)]. The rate is

$$v = k[\mathrm{PhCH_2NHPh}][\mathrm{MeOI}] \qquad (3)$$

expressed as equation (4) for a small excess of alkali over iodine, since a plot of k_{obs} *vs.* $[\mathrm{I_2}]_t^{-1}$ (Figure 2) affords a straight line with slope proportional to $[\mathrm{MeO^-}]_t$ (total concentration of added sodium methoxide) (Table 3).

$$v = k_{\mathrm{obs}}[\mathrm{PhCH_2NHPh}] = k'[\mathrm{PhCH_2NHPh}]([\mathrm{MeO^-}]_t/[\mathrm{I_2}]_t - 1) \qquad (4)$$

The k' value obtained from the slope is consistent with that from the intercept of the line.

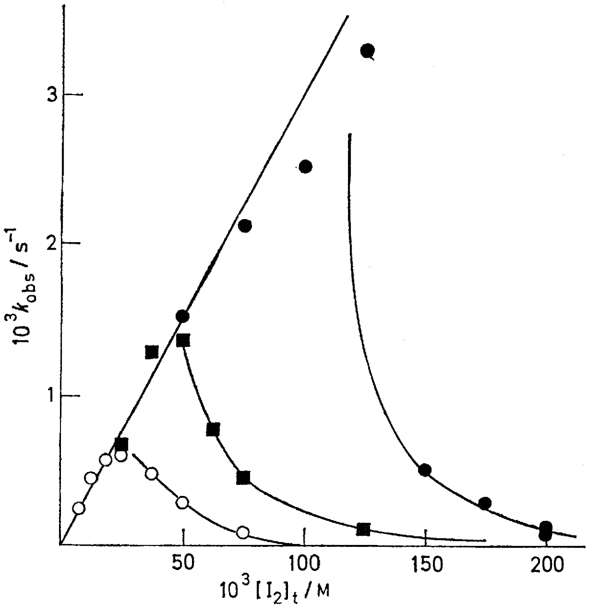


FIGURE 1 Correlation of observed rate constant with concentration of added iodine $[\mathrm{I_2}]_t$: ● $[\mathrm{NaOMe}]_t = 0{\cdot}5$M; ■ $[\mathrm{NaOMe}]_t = 0{\cdot}2$M; ○ $[\mathrm{NaOMe}]_t = 0{\cdot}1$M

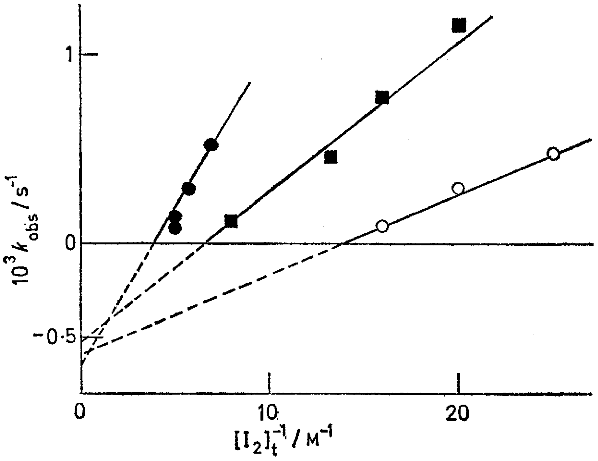


FIGURE 2 Plot of observed rate constant against $[\mathrm{I_2}]_t^{-1}$: ● $[\mathrm{NaOMe}]_t = 0{\cdot}5$M; ■ $[\mathrm{NaOMe}]_t = 0{\cdot}2$M; ○ $[\mathrm{NaOMe}]_t = 0{\cdot}1$M

Substituent Effect.—The rates of reaction of some ring-substituted *N*-benzylanilines with a mixture of iodine and a large excess of sodium methoxide were measured in methanol at 25° and the results are summarised in Table 4.

TABLE 3

Effect of concentration of added methoxide on the slope of the plot of k_{obs} against $[\mathrm{I_2}]_t^{-1}$ in Figure 2

$[\mathrm{NaOMe}]_t$/M	$10^4 k'$/s^{-1} [a]	$10^4 k'$/s^{-1} [b]
0·5	3·57	6·35
0·2	3·60	5·52
0·1	3·60	5·59

[a] Value obtained from the slope of a plot of k_{obs} against $[\mathrm{I_2}]_t^{-1}$, *i.e.*, $k_{\mathrm{obs}} = k'([\mathrm{NaOMe}]_t/[\mathrm{I_2}]_t - 1)$. [b] Value obtained from the intercept.

TABLE 4

Substituent effect on the reaction of *N*-benzylanilines with iodine in methanolic sodium methoxide at 25°

$\mathrm{YC_6H_4CH_2NHC_6H_4Z}$		k_{rel}	log k_{rel}
Y	Z		
H	*p*-MeO	2·28	+0·358
H	*p*-Me	1·44	+0·175
H	H	1	0
H	*p*-Cl	0·562	−0·251
H	*m*-Cl	0·370	−0·432
p-Me	H	0·824	−0·084
p-Cl	H	1·316	+0·120
m-Cl	H	1·326	+0·123

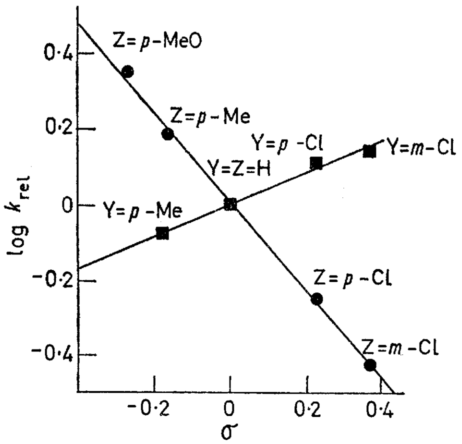


FIGURE 3 Hammett plot for the reaction of *N*-benzylanilines ($\mathrm{YC_6H_4CH_2NHC_6H_4Z}$) with iodine in alkaline methanol at 25°

The kinetic substituent effects are correlated by Hammett σ values and give a ρ_{Y} value of +0·38 for substituents (Y) in the benzyl ring and a ρ_{Z} value of −1·15 for substituents (Z) in the aniline ring. Thus, an electron-attracting group in the benzyl ring increases the rate, but when in the aniline ring decreases the rate.

DISCUSSION

Exclusion of the Intermediacy of N-*Benzyl*-N-*halogenoaniline.*—Bachmann [3a] postulated a mechanism for the reaction of amines bearing an α-hydrogen atom with hypohalite and alkali which involves the initial formation of an *N*-halogenoamine (III) followed by dehydrohalogenation with a base to give an imine (IV) (Scheme 1).

However, since reaction (5) is reversible, as suggested by Gassman,[5a] (III) may not be an intermediate, but

[5] (*a*) P. G. Gassman and G. A. Campbell, *J. Amer. Chem. Soc.*, 1972, **94**, 3891; (*b*) R. S. Neale, R. G. Schepers, and M. R. Walsh, *J. Org. Chem.*, 1964, **29**, 3390.

only a byproduct in the formation of (IV). The intermediacy of an *N*-halogenoamine (III) is excluded by the

$$\underset{\text{(I)}}{R^2CH_2NHR^3} + \underset{\text{(II)}}{R^1OX} \rightleftharpoons \underset{\text{(III)}}{R^2CH_2NXR^{3\prime}} + R^1OH \quad (5)$$

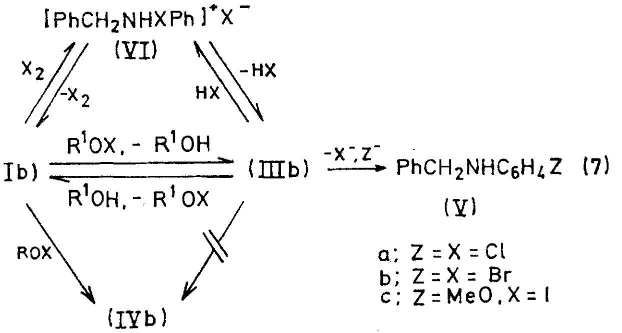
a; $R^2 = R^3$ = H or alkyl
b; $R^2 = R^3$ = phenyl

a; X = Cl
b; X = Br
c; X = I

$$\text{(III)} + R^1O^- \longrightarrow \underset{\text{(IV)}}{R^2CH{=}NR^3} + R^1OH \quad (6)$$

Scheme 1

following facts. (i) *N*-Benzyl-*N*-chloroaniline (IIIb; X = Cl) which should be formed from *N*-benzylaniline (Ib) on treatment with t-butyl hypochlorite [3a] or calcium hypochlorite [5a] produces *o*- and *p*-chloro-*N*-benzylanilines (Va) together with other products. (ii) *N*-Bromo- and *N*-chloro-*N*-benzylaniline hydrohalides (VI; X = Br and Cl), which must be in equilibrium with (IIIb), give no (IVb) but only (Va and b) and (Ib) on addition of sodium methoxide in methanol. (iii) Although *N*-benzyl-*N*-iodoanilinium iodide (VI; X = I) could not be prepared by treatment of *N*-benzylaniline (Ib) with iodine, the reaction of (Ib) with iodine in methanol at 64° in the absence of sodium methoxide gave *N*-benzyl-*p*-methoxyaniline which must be derived from *N*-benzyl-*N*-iodoaniline (IIIb).[5a] Thus it is certain that *N*-halogeno-*N*-benzylanilines gives *o*- and *p*-halogeno(or methoxy)-*N*-benzylanilines, whereas (Ib) produces no (V) but only (IVb) on addition of hypohalite in alkali if [MeO$^-$] > [MeOX]. Therefore, the formation of (IV) should occur *via* direct attack of hypohalite on (I) (Scheme 2).



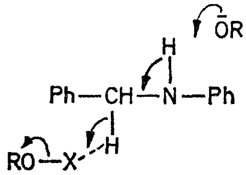
Scheme 2

Mechanism in Highly Basic Solution.—Halogens can exist in the forms X_2, X_3^-, and MeOX in methanol, the concentrations depending on the basicity of the solution. The oxidant of the conversion of amine into imine in highly basic solution should be hypohalite for the following reasons. (i) Halogen should be converted almost completely into hypohalite in alkaline solution (the equilibrium constants in aqueous solution K_8 at 25° are 10^{15} for Cl_2, 10^8 for Br_2, and 20—200 for I_2).[6] (ii) Compounds (III) and (VI), which are formed by the reaction

$$X_2 + RO^- \underset{}{\overset{K_8}{\rightleftharpoons}} ROX + X^- \quad (8)$$

of (I) with molecular halogen, and which are in equilibrium [equation (7)], do not give imine on treatment of alkali. (iii) t-Butyl hypochlorite, which can give neither Cl_2 nor Cl_3^- (with Cl^-) in alkaline solution, reacts similarly with amine (I) to give imine (IV) as in the case of molecular halogen in alkaline solution.

A mechanism involving abstraction of a benzylic hydride ion as in the bromine oxidation of alcohols (Scheme 3) [6] is excluded, because electron-attracting substituents on the benzyl ring increase the rate in contrast to the bromine oxidation of benzyl alcohol.[7] Hence, abstraction of a benzylic proton is probable.



Scheme 3

The rate equation (3) can be interpreted as requiring that a molecule each of *N*-benzylaniline and hypohalite, but not methoxide ion, should participate in the rate-determining step. The reaction of the anions from *N*-benzylaniline [(VII) and (VIII)] with hypohalite is not involved in the mechanism, because the observed rate is independent of the concentration of the base and because the equilibrium constants [8] K_9 and K_{10} may be $<10^{-20}$.

$$\text{(Ib)} + R^1O^- \overset{K_9}{\rightleftharpoons} \underset{\text{(VII)}}{PhCH_2\bar{N}Ph} + R^1OH \quad (9)$$

$$\text{(Ib)} + R^1O^- \overset{K_{10}}{\rightleftharpoons} \underset{\text{(VIII)}}{Ph\bar{C}HNHPh} + R^1OH \quad (10)$$

Our kinetic observation and other facts can only be explained by Scheme 4. If equation (11) is the slow step, the rate law is expressed as $v = k_{11}[\text{(Ib)}][\text{(II)}]$, which is the case. This mechanism is supported by substituent effects (see Results section), an electron-attracting group on the aniline ring decreasing the rate of nucleophilic attack on nitrogen and on the benzyl ring favouring the elimination of a benzylic proton. These opposing effects decrease both ρ values, although one (that in the aniline ring) is more pronounced than the other. Recently, Lee [1e] reported a negative ρ value for the reaction of benzyldimethylamine with bromine in acid to produce benzaldehyde and dimethylamine and suggested a mechanism which involves loss of a benzyl proton in the rate-determining step. The intermediate α-halogenobenzylamines (XI) were isolated

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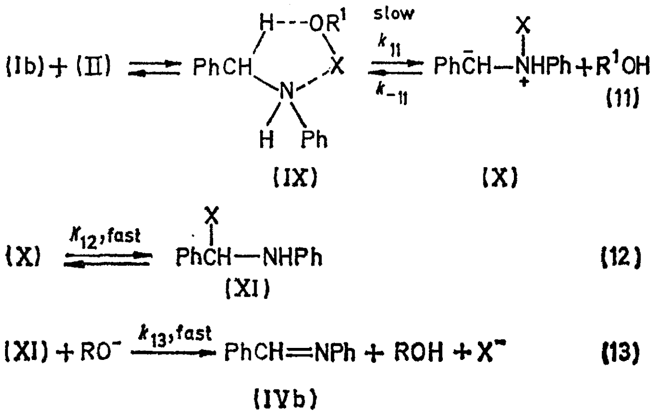
[6] (*a*) A. Skrabal, *Monatsh*, 1911, **32**, 167 (*Chem. Abs.*, 1911, **5**, 2591); (*b*) Y. Chia, U.S. Atomic Energy Commission, 1958, UCRL-8311, p. 87 (*Chem. Abs.*, 1958, **53**, 2914e); (*c*) C. H. Li, *J. Amer. Chem. Soc.*, 1947, **64**, 1147.

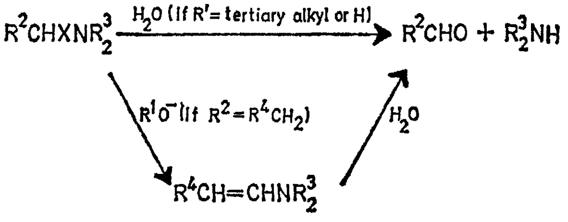
[7] (*a*) P. Aukett and I. R. L. Barker, *J.C.S. Perkin II*, 1972, 568; (*b*) B. Perlmutter-Hayman and Y. Weissmann, *J. Amer. Chem. Soc.*, 1969, **91**, 668.

[8] D. J. Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1965, p. 41.

as reported for tertiary amines[1b] which are converted into enamines[1a] or carbonyl compounds (Scheme 5).



SCHEME 4



SCHEME 5

Mechanism in Weakly Basic Solution.—As shown in Figure 1, increasing the amount of added iodine suppresses the rate at the point where the concentration of the remaining iodine is comparable with that of *N*-benzylaniline (Ib), if K_8 is *ca.* 30—50 (as in aqueous solution).[6]

Molecular chlorine and bromine react with *N*-benzylaniline (Ib) to give *N*-halogenoamine (IIIb) and *N*-halogenoaminium halide (VI) which are converted slowly into *o*- and *p*-halogenoanilines (Va and b) [equation (7)]. Although (IIIb; X = I) and (VI; X = I) could not be isolated in the case of iodine, it is clear that (Ib) forms a complex with iodine similar to (III) or (VI) which resists the direct conversion into imine (IVb), because (Ib) reacts with molecular iodine to give *N*-benzyl-*p*-methoxyaniline (Vc). Since iodine has a lower ionization potential, the complex probably has charge-transfer nature (XII) rather than being of the form (III) or (VI). The complex (XII) will not be isolated as a precipitate from an ethereal solution as in the case of (VI), but will be converted into (Vc). Since K_{14} is

$$\text{(Ib)} + \text{I}_2 \xrightleftharpoons{K_{14}} \underset{\text{(XII)}}{[\text{PhCH}_2\overset{\delta+}{\text{N}}\text{HPh}]\overset{\delta-}{\text{I}_2}} \qquad (14)$$

large (a value of 6300—6700 was reported for the formation of the charge-transfer complex between secondary amines and iodine[9]), the rate may be expressed by equation (15) assuming equation (11) is the slow step. Here,

$$v = k_{11}[\text{(Ib)}][\text{MeOI}] = k_{11}[\text{(XII)}][\text{MeOI}]/K_{14}[\text{I}_2] \qquad (15)$$

$[\text{I}_2]$ is the concentration of the remaining molecular iodine and $[\text{(XII)}]$ is nearly equal to $[\text{(Ib)}]_m$ [observed concentration of (Ib)]. Consequently, equation (15) reduces to (16). $[\text{MeOI}]/[\text{I}_2]_t \fallingdotseq 1$, and $[\text{I}_2]_t$ is approximately equal

$$v = k_{11}[\text{(Ib)}]_m[\text{MeOI}]/K_{14}[\text{I}_2] \qquad (16)$$

to $[\text{I}_2]_t^2/K_8([\text{MeO}^-]_t - [\text{I}_2])_t$, when $[\text{MeO}^-]_t > [\text{I}_2]_t$. Hence equation (16) is converted into (17). This equation agrees with the experimentally derived equation (4).

$$v = \frac{k_{11}K_8[\text{(Ib)}]_m}{K_{14}}\left(\frac{[\text{MeO}^-]_t}{[\text{I}_2]_t} - 1\right) \qquad (17)$$

[3/2097 *Received*, 15*th October*, 1973]

[9] (*a*) H. Yada, J. Tanaka, and S. Nagakura, *Bull. Chem. Soc. Japan*, 1960, **33**, 1660; (*b*) M. S. Mulliken and W. S. Person, 'Molecular Complexes,' Wiley-Interscience, New York, 1969, p. 154.