Mechanism of Oxidative Cleavage by Bromine of Diazabutadienes (Azines) to Aldehydes or Ketones

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2,3-Diazabuta-1,3-dienes (1; $R = Me$ or H) are smoothly cleaved by bromine in 7 : 3 acetic acid–water at 25° to give quantitative amounts of the corresponding substituted acetophenone(s) or benzaldehyde(s) with the evolution of nitrogen. Kinetic studies under these conditions show that two moles of bromine are consumed per mole of (1) oxidized; one mole of bromine is involved at or before the rate-determining step while the second mole reacts rapidly in a subsequent step. Surprisingly, electron-donating substituents slow and electron-withdrawing substituents enhance the reactivity of (1) (Hammett ρ +0.8 when $R = H$ and +0.32 when $R = Me$) which is unexpected for a reaction involving electrophilic attack by bromine. A mechanism is proposed in which a small equilibrium concentration of the hydrate (6) is formed; the reaction of (6) with bromine [to give the diazoalkane (9)] is rate determining. The second mole of bromine reacts with the diazoalkane (9) which is shown independently to react rapidly, yielding the ketone (11).

THE chlorination of 2,3-diazabuta-1,3-dienes (1) to give $\alpha\alpha'$-dichloroazoalkanes (2) was first described by Benzing[1] and by Goldschmidt.[2] The reaction, which is carried out at low temperature usually in the absence of solvent, was shown by Malament and McBride[3] to be ionic. Stolle had earlier reported[4,5] that with 1,4-unsubstituted materials (1; $R = H$) chlorination in carbon tetrachloride at 0° leads to a replacement product (3). Disubstitution is also possible [formation of (4)] either on prolonged chlorination in carbon tetrachloride or when acetic acid is used as solvent (at room temperature).[6] The corresponding bromination reactions are less well documented, but previous studies have indicated that when $R = H$, bromination of (1) in acetic acid leads to azinium perbromides.[7]

We have examined the mechanism of these reactions using bromination in acetic acid–water as a model. Under these conditions we have found that the azines (1) are cleanly oxidized to regenerate the starting aldehyde or ketone and nitrogen is released. Under the mild conditions used no accompanying nuclear or α- (in the case of ketone derivatives) bromination was observed. The alternative methods which can be used for the cleavage of azines are more severe (*e.g.* use of 1M-acid at elevated

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[1] E. Benzing, *Annalen*, 1960, **631**, 1, 23.

[2] S. Goldschmidt and B. Acksteiner, *Annalen*, 1958, **618**, 173; *Chem. Ber.*, 1958, **91**, 502.

[3] D. S. Malament and J. M. McBride, *J. Amer. Chem. Soc.*, 1970, **92**, 4586, 4593.

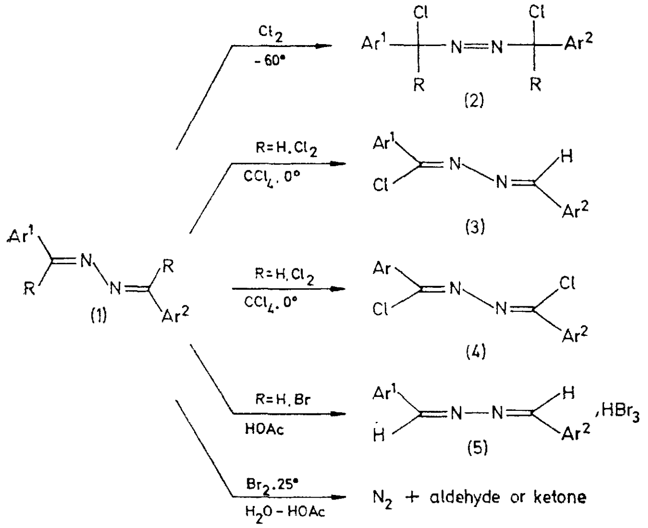
[4] R. Stolle and F. Helwerth, *Ber.*, 1914, **47**, 1132.

[5] R. Stolle, *J. prakt. Chem.*, 1912, **85**, 386.

[6] A. F. Hegarty, J. Cronin, P. A. Cashell, and F. L. Scott, *J.C.S. Perkin II*, 1973, 1708.

[7] F. L. Scott and P. A. Cashell, *J. Chem. Soc. (C)*, 1970, 2674.

temperatures) and this has previously restricted the use of these materials as intermediates for the protection or purification of aldehydes and ketones.



RESULTS AND DISCUSSION

(a) *Stoicheiometry of Bromination.*—Using various initial [bromine] : [azine] ratios it was clearly established that in 7 : 3 acetic acid–water in all cases two moles of bromine were consumed per mole of azine oxidized. This was true independent of whether the substrate was an aldazine (1; R = H) or a ketazine (1; R = Me). When a 1 : 1 molar ratio was used experiments carried out on a large scale showed that *ca.* 50% of the azine was oxidized while the remainder was unaffected.

It is unlikely that three molecules (2 Br_2 and azine) are involved in the rate-determining step (true termolecular reactions are rare) [8] and this was confirmed when the kinetics of bromination were examined. The results for benzaldehyde azine (1; $Ar^1 = Ar^2 = Ph$, R = H) are summarized in Table 1. The second-order rate constant (k_2) was calculated using equation (1) which was derived by assuming that the rate-determining step involves one mole of bromine and one mole of azine; the second mole of bromine is consumed rapidly *after* the slow step (a = initial concentration of azine, b = initial concentration of bromine, x = molar concentration of azine which has reacted at time t, $2x$ = molar concentration of bromine which has reacted at time t). To simplify the calculations, an excess of bromine was generally used (*i.e.* $b > 2a$); since the bromine was electrogenerated, the quantity of azine could then be accurately titrated. The same rate constant (k_2) was obtained when (a) the initial concentration of bromine was exactly twice that of the azine or (b) when the azine was in a 20-fold excess, providing further evidence for the validity of equation (1). The reaction was also insensitive to the presence or absence of light.

$$k_2 = \frac{2.303}{(2a - b)t} \log \frac{b(a - x)}{a(b - 2x)} \qquad (1)$$

TABLE 1

Second-order rate constants for the bromination of benzaldehyde azine (1; R = H, $Ar^1 = Ar^2 = Ph$) in 7 : 3 acetic acid–water (at 25° in the presence of 0.10M-KBr)

10^5[Azine]/M	10^5[Bromine]/M	k_2/l mol^{-1} s^{-1}
2.0	6.0	260
2.0	5.0	262
0.5	1.5	275
2.0	7.0	276

(b) *Substituent Effects.*—The presence of substituents in the aryl rings Ar^1 and Ar^2 in (1; R = H) has a marked effect on reactivity (Table 2). The most surprising aspect of these data is the observation that electron-withdrawing substituents enhance and electron-donating substituents slow the overall reaction. On this basis a simple mechanism involving rate-determining attack by electrophilic bromine can be ruled out. Thus the Hammett ρ value obtained from the data of Table 2 (the sum of the McDaniel–Brown [9] σ values for the two substituents was used) is +0.81 (r 0.998). However in typical electrophilic side-chain brominations ρ is invariably negative (indicating, as expected, the build up of *positive* charge on the substrate in the transition state); values reported are −3.57 for monosubstituted diphenylethylenes,[10] −0.62 for arylidenehydrazones.[11]

TABLE 2

Second-order rate constants for the bromination of aldazines (1; R = H, $Ar^1 = Ar^2$) in 7 : 3 acetic acid–water (at 25° in the presence of 0.10M-KBr)

$Ar^1 = Ar^2$	k_2/l mol^{-1} s^{-1}
Ph	260
p-ClC_6H_4	114
p-MeC_6H_4	130
p-$Me_2CHC_6H_4$	146
m-MeC_6H_4	229
p-$MeOC_6H_4$	25.3
p-FC_6H_4	281
p-$NO_2C_6H_4$	5 280
m-$NO_2C_6H_4$	3 780
m-ClC_6H_4	914

These results are however paralleled by data for ketazines (Table 3). In this case, (1; R = Me), both symmetrical ($Ar^1 = Ar^2$) and unsymmetrical materials ($Ar^1 \neq Ar^2$) were studied. Overall the ketazines react *ca.* 10-fold less rapidly than the corresponding aldazines and the sensitivity throughout the series is somewhat smaller. Thus a plot of log k_2 against Σσ for symmetrically disubstituted ketazines gave ρ +0.32. There is some scatter if an attempt is made to correlate the data for the unsymmetrical materials (1; $Ar^1 \neq Ar^2$, R = Me) on this plot. However the correlations are

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[11] A. F. Hegarty and F. L. Scott, *J. Chem. Soc.* (*B*), 1966, 6 7

improved when the substrates with a constant p-$NO_2C_6H_4$ or p-MeC_6H_4 substituent are grouped together [ρ +0.37 (r 0.997) and +0.28 (r 0.997) respectively].

(c) *Product Analysis.*—As mentioned at the outset, nitrogen gas was evolved on treatment of both aldazines (1; R = H) and ketazines (1; R = Me) with bromine in 7 : 3 acetic acid–water at 25°. The quantity of nitrogen was estimated using a gas burette; the theoretical quantity (±10%), assuming one mole N_2 per mole of azine, was evolved in all cases.

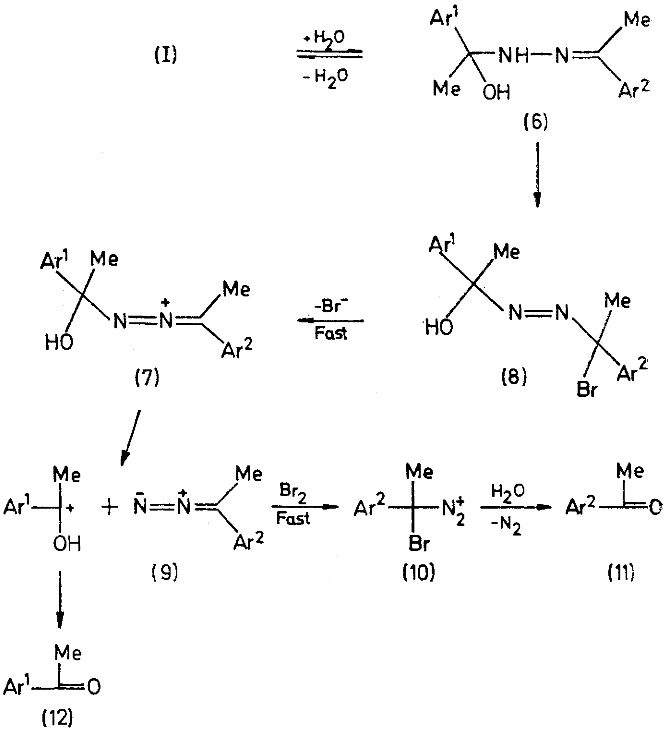
TABLE 3

Second-order rate constants for the bromination of ketazines (1; R = Me) in 7 : 3 acetic acid–water (at 25° in the presence of 0.10M-KBr)

Ar^1	Ar^2	k_2/l mol^{-1} s^{-1}
p-$NO_2C_6H_4$	p-$NO_2C_6H_4$	129
p-$NO_2C_6H_4$	p-MeC_6H_4	36
p-$NO_2C_6H_4$	p-ClC_6H_4	53
p-$NO_2C_6H_4$	Ph	44
p-MeC_6H_4	p-MeC_6H_4	14
m-ClC_6H_4	m-ClC_6H_4	37
p-BrC_6H_4	p-BrC_6H_4	33
m-BrC_6H_4	m-BrC_6H_4	38
p-ClC_6H_4	Ph	32
m-ClC_6H_4	p-ClC_6H_4	33
Ph	Ph	20
m-$NO_2C_6H_4$	m-$NO_2C_6H_4$	55

T.l.c. indicated that the corresponding aldehyde or ketone was also formed. This was confirmed by the addition of p-nitro- or 2,4-dinitro-phenylhydrazine to the reaction mixture on completion of nitrogen evolution and estimation of the hydrazones formed. Typically 92% p-bromo-acetophenone and 96% p-nitroacetophenone p-nitrophenylhydrazone (based on two moles of ketone per mole of azine) were recovered. Control experiments under the same conditions indicate that these values represent *ca.* 100% ketone (aldehyde) formation during the oxidative bromination. G.l.c. and t.l.c. analysis indicated that no appreciable amounts of the corresponding alcohols [*e.g.* 1-phenylethanol from (1; $Ar^1 = Ar^2$ = Ph, R = Me)] were present.

(d) *Mechanism.*—A possible mechanism of oxidative bromination is suggested in Scheme 1 to account for these observations. Nucleophilic attack on the azine (1) yields a small equilibrium concentration of the hydrazone (6) which is trapped by reaction with bromine [11,12] at the carbon adjacent to Ar^2 to yield (on proton loss) the azo-intermediate (8). The α-halogeno-α′-hydroxy-material (8) is analogous to the proposed intermediate in the hydrolysis of αα′-dichlorodiazoalkanes [2] and should undergo rapid bromide ion loss [*via* the stabilized aza-allene (7)] to give the ketone (12) and diazoalkane (9). The latter reacts rapidly with water to give the ketone (11). It is well established [13] that diazoalkanes give alcohols in acidic aqueous solution; nevertheless no alcohol products were detected in the present instance. However, the reaction medium contains the electrophile bromine and this could react with (9) at carbon in a manner analogous to the proton. There are few data available on the halogenation of diazoalkanes; [14] however, we have found that the reaction is rapid and the major (or sole) product is the corresponding ketone (11) in 7 : 3 acetic acid–water. Thus 98% p-nitroacetophenone (isolated as the p-nitrophenylhydrazone) was obtained when p-nitrophenyldiazoethane (9; Ar^2 = p-$NO_2C_6H_4$) was treated with an equimolar quantity of bromine under these conditions. Similarly p-bromoacetophenone (92%) was obtained from p-bromophenyldiazoethane. Kinetic studies showed that the reactions of bromine with diazoalkanes were very rapid, being in all cases faster than the initial reaction of the azine (1). Moreover, the characteristic diazoalkane colour was not apparent during the course of the bromination of (1). The observed formation of two moles of ketone [(11) + (12)] per mole of azine and the rapid consumption of a second mole of bromine after the rate-determining step is therefore consistent with the presence of the diazoalkane (9) on the reaction pathway.



SCHEME 1

The small positive ρ values observed for substituents in Ar^1 and Ar^2 (implying the build up of negative charge in the transition state) rules out direct electrophilic attack by halogen on (1) as the rate-determining step. Uncatalysed reaction of (1) with water (or acetate ion or possibly bromide ion) would be characterised by a positive ρ value in the range +1 to +3 as shown by the basic hydrolysis of azines and imines.[6] Since the direct hydrolysis of azines in neutral solution is slow, the equi-

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[14] G. W. Cowell and A. Ledwith, *Quart. Rev.*, 1970, **24**, 119.

librium concentration of (6) is expected to be low; this should be balanced however by the high reactivity of (6) towards bromine. Moreover, since the electrophilic step [(6) $\longrightarrow$ (8)] is characterised by a small negative ρ value (—0.62 for substituents in Ar^2) the overall reaction should show a small but positive ρ (as observed.)

Several alternative species were considered as possible intermediates which might have consumed the second mole of bromine and led to ketones (11) and (12). These included 1-arylethanols (13), arylidene dibromides (14), *N'*-arylidenebenzohydrazides (15), and 2,5-diphenyl-1,3,4-oxadiazole (16). Neither (13) nor (16) reacted at an appreciable rate with bromine; (14; Ar = Ph) was actually solvolysed to the corresponding aldehyde in 7 : 3 acetic acid–water. Thus 5% benzaldehyde was obtained after 15 min and 58% after 4.5 h. However the bromination of benzaldehyde azine (1; $Ar^1 = Ar^2 = Ph$, R = H) has a half-life of *ca.* $<$30 s and all the aldehyde was released when the analysis was completed in 15 min. Thus (14; Ar = Ph) cannot be an intermediate in the reaction of (1). Similar results were obtained with p-nitrobenzylidene dibromide (14; Ar = p-$NO_2C_6H_4$) which did not undergo appreciable solvolysis in the reaction medium whereas the corresponding azine (1; $Ar^1 = Ar^2 = p$-$NO_2C_6H_4$, R = H) is rapidly oxidized to the aldehyde (Table 2).

$Ar(Me)CHOH$

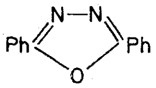
(13)

$ArCHBr_2$

(14)

$ArCH{=}N{-}NHCOPh$

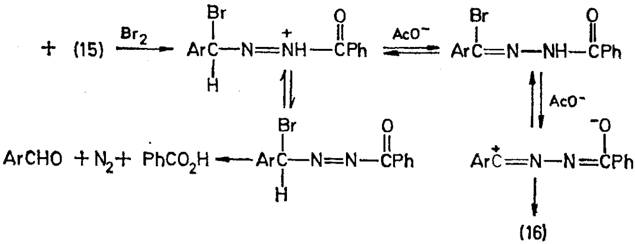
(15)



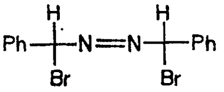
(16)

The kinetics of bromination of the benzohydrazides (15) was examined in some detail since these materials are formed on solvolysis of the monochlorides[6] (3) (and thus presumably the corresponding monobromides). A Hammett plot of the second-order rate constants *versus* the σ value of the substituent in Ar^1 gave ρ —0.94 (r 0.992). This value is typical for a reaction involving rate-determining electrophilic attack by bromine on (15).[11] However bromination of (15; Ar = Ph) was considerably slower than that of benzaldehyde azine under the same conditions; moreover the products obtained on bromination of (15) in 7 : 3 acetic acid–water were the aldehyde (ArCHO) and an equimolar quantity of benzoic acid. When (15) was brominated in the presence of two equivalents of sodium acetate, the product was the oxadiazole (16); a possible mechanism is outlined in Scheme 2.

An attempt was made to isolate a brominated azine (17) by carrying out the bromination of benzaldehyde azine under anhydrous conditions. At room temperature in acetic acid the salt (5; $Ar^1 = Ar^2 = H$) was obtained. When brominated in acetic acid at reflux (in the presence of excess of bromide ion) *meso*-stilbene dibromide (18) was formed in 14% yield. This provides evidence for the intermediacy of (17) since the corresponding chlorides (2; R = Me) are known[2] to give stilbene dichlorides on heating to 120°. An alternative route to (18) *via* preliminary thermolysis of benzaldehyde azine to stilbene can be ruled out since thermolysis even at 210° is slow.[15]

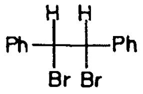


SCHEME 2



$$Ph{-}\overset{H}{\underset{Br}{C}}{-}N{=}N{-}\overset{H}{\underset{Br}{C}}{-}Ph$$

(17)



$$Ph{-}\overset{H}{\underset{Br}{C}}{-}\overset{H}{\underset{Br}{C}}{-}Ph$$

(18)

Thus, in summary, the oxidative cleavage of the azines (1) by bromine in aqueous acetic acid is best represented as occurring *via* the rate-determining formation of a diazoalkane intermediate (9). The latter rapidly loses nitrogen to form a ketone (or aldehyde) on reaction with a second mole of bromine.

EXPERIMENTAL

Substrates.— 1,4-*Diaryl*-1,4-*dimethyl*-2,3-*diazabuta*-1,3-*dienes*. The symmetrically disubstituted ketazines (1; $Ar^1 = Ar^2$, R = Me) were prepared by the reaction of hydrazine hydrate (1 mol. equiv.) with the appropriate substituted acetophenone (2 mol. equiv.) in 95% ethanol and recrystallized to constant m.p. in this solvent. The unsymmetrical materials (1; $Ar^1 \neq Ar^2$, R = Me) were synthesized[16] from the corresponding p-nitroacetophenone, p-chloroacetophenone, or m-nitroacetophenone hydrazone and an equimolar quantity of the substituted acetophenone. Physical data for the ketazines has previously been recorded.[17] Only symmetrically disubstituted aldazines (1; $Ar^1 = Ar^2$; R = H) were used; these were prepared analogously to the ketazines: aldazines (1; R = H, $Ar^1 = Ar^2 = XC_6H_4$); X = p-MeO, m.p. 168—170° (lit.,[18] 170°); p-Me, 153° (lit.,[19] 153°); p-Pr^i, 109—110° (lit.,[20] 109—110°); H, 93° (lit.,[21] 92—93°); p-F, 185—187° (lit.,[22] 185°); p-Cl, 209—210° (lit.,[23] 206.5—207°); p-Br, 223.5—224.5 (lit.,[24] 223.5—224.5°); m-Cl, 146° (Found: C, 60.5; H, 3.7; N, 10.2. $C_{14}H_{10}Cl_2N_2$ requires C, 60.6; H, 3.6; N, 10.12); p-NO_2, 297° (lit.,[18] 302°); m-NO_2, 196° (Found: C, 56.65; H,

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3.5; N, 18.6. $C_{14}H_{10}N_4O_4$ requires C, 56.4; H, 3.35; N, 18.8%); *m*-Me, 74° (Found: C, 82.0; H, 7.1; N, 12.1. $C_{16}H_{16}N_2$ requires C, 81.4; H, 6.8; N, 11.9%).

Substituted N′-*Arylidenebenzohydrazides* (15).—These materials were synthesized by the condensation of the substituted benzaldehyde with benzohydrazide (equimolar quantities) in ethanol. The following materials were prepared: Ar = *p*-XC_6H_4; X = H, m.p. 204—205° (lit.,[25] 206°), NO_2, 240° (lit.,[26] 243°); MeO, 158—160° (lit.,[26] 158°); Me, 154—155° (lit.,[27] 155°).

Benzylidene dibromide was prepared by the method of Coleman and Honeywell,[28] and had b.p. 132—134° at 36 mmHg, n_D^{20} 1.610 (lit.,[29] 1.615). *p*-Nitrobenzylidene dibromide was similarly prepared, m.p. 82° (lit.,[30] 82—82.5°).

Chlorination of 1,4-*Diphenyl*-2,3-*diazabuta*-1,3-*diene*.—The azine (1; $Ar^1 = Ar^2$ = Ph, R = H) was treated in the absence of solvent at −60°, according to the method used by Benzing [1] for the synthesis is 1,1′-dichloroazoalkanes (2). The product isolated was recrystallized from n-pentane and had m.p. 56—57° (51%); analysis and mixed m.p. showed this to be the monochloro-material (3; $Ar^1 = Ar^2$ = Ph) (lit.,[4] m.p. 57°).

Bromination of p-*Nitrophenyldiazoethane*.—*p*-Nitrophenyldiazoethane (0.44 g) in dry ether (15 ml) was added to 7 : 3 acetic acid–water (30 ml) containing bromine (0.15 ml, 1.1 equiv.) and potassium bromide (0.1M). The bromine colour was discharged and effervesence noted. After 10 min, water (50 ml) was added and the suspension extracted with ether. The oil (0.36 g) obtained on evaporation of the dried ether extracts was largely *p*-nitroacetophenone, $\nu_{max.}$ 1 685 cm^{-1} [t.l.c. analysis on alumina using n-pentane–chloroform (4 : 1) as mobile phase]. A sample of the oil (0.11 g) was treated with hydrazine hydrate in 95% ethanol (10 ml) and refluxed for 0.5 h. Upon cooling *p*-nitroacetophenone hydrazone (0.115 g, 86%, based on diazoethane) crystallized out, m.p. and mixed m.p. with an authentic sample 146—151°. A similar recovery was observed with *p*-nitro- and 2,4-dinitrophenylhydrazones. *p*-Bromophenyldiazoethane (prepared from *p*-bromoacetophenone hydrazone [16]) was reacted with bromine under the same conditions. The *p*-bromoacetophenone formed was recovered directly and had m.p. 48—52° (84% yield).

Bromination of 1,4-*Dimethyl*-1,4-*bis*-(p-*nitrophenyl*)-2,3-*diazabuta*-1,3-*diene*.—The azine (1; $Ar^1 = Ar^2$ = *p*-$NO_2C_6H_4$, R = Me) (3.26 g) was stirred in 7 : 3 acetic acid–water and bromine (1.0 ml) in acetic acid (10 ml) was added dropwise over 1 h at ambient temperature. Stirring was continued for a further 4 h when a clear yellow solution was obtained. The solution was shown to be free from bromine (starch–iodide paper) and was filtered to remove a small amount of unchanged azine. The filtrate was added to acetic acid (50 ml) and phenylhydrazine (2.66 ml) was added to give *p*-nitroacetophenone phenylhydrazone (4.4 g, 91%), m.p. 131° (lit.,[31] 132°). *p*-Bromoacetophenone was similarly isolated as a phenylhydrazone (87%), m.p. 119—120° (lit.,[31] 120°) in the reaction of 1,4-bis-(*p*-bromophenyl)-1,4-dimethyl-2,3-diazabuta-1,3-diene with bromine under the same conditions.

The product ketones were also estimated using g.l.c. (Pye series 104 Chromatograph with 1 m 15% PEGA on 60—72 Celite) using chlorobenzene as standard. The column temperature was in the range 180—220°. The yields of aldehydes obtained on extraction of the aqueous acetic acid solutions of (1; $Ar^1 = Ar^2 = XC_6H_4$, R = H) on completion of reaction with bromine are as follows: X = H, 69% benzaldehyde; X = *p*-F, 88% *p*-fluorobenzaldehyde; X = *p*-Cl, 98% *p*-chlorobenzaldehyde; *p*-Me, 80% *p*-tolualdehyde; *p*-Pr^i, 79% *p*-isopropylbenzaldehyde.

Kinetic Method.—The rates of bromination were studied in 7 : 3 acetic acid–water containing 0.1M-KBr at 20 or 25° using an electrometric method to detect low concentrations of bromine. Acetic acid was purified by reflux over chromium trioxide by the method of Orton and Bradfield; [32] the water was twice distilled from alkaline potassium permanganate. The apparatus used (which incorporated a coulometer to generate bromine by electrolysis of the potassium bromide) [33] has already been described in detail.[11]

When the initial azine concentration was greater than that of bromine (*i.e.* $b > 2a$) then the bromine concentration–time plot could be calibrated to give the various parameters $b - 2a$, $a - x$, $b - 2x$. Plots of log $(a - x)$ − log$(b - 2x)$ against time were linear; the second-order rate constants were then calculated from the slopes of these plots using equation (1). In each case the kinetic experiments were replicated at least twice and the values quoted (Tables 1—3) are the mean values (±4%).

In preliminary experiments, a second-order dependence on bromine concentration was ruled out by carrying out the reaction with the initial bromine concentration exactly twice that of the azine. Under these conditions for an overall third-order reaction (rate = k_{obs} [Azine][Bromine] ^{2}) a plot of $[Br_2]^{-2}$ against time should be linear. However such plots were shown to give very poor correlations (r) typically in the range 0.19—0.82 using the least squares method by means of an IBM 1130 computer. Plots of $[Br_2]^{-1}$ against time however were linear ($r > 0.994$) under the same conditions, implying a first-order dependence on bromine.

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