Synthesis of Aliphatic Hydrazonyl Bromides and Kinetics of their Conversion into Hydrazides

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The hydrolytic conversion of *N*-(4-nitrophenyl)-, *N*-(2-bromo-4-nitrophenyl)-, and *N*-(2,4-dinitrophenyl)-alkanohydrazonyl bromides into the corresponding alkyl hydrazides has been investigated kinetically in 80% aqueous dioxan. The rates of hydrolysis for all three series of compounds were found to decrease with increasing alkyl substitution. This was attributed to the bulk of the alkyl group retarding solvolysis, since electron-withdrawing groups strongly retard reaction. Further evidence (large solvent, common-ion, and salt effects) also supports a mechanism involving rate-determining unimolecular ionization. The reaction of benzenediazonium ion with the parent hydrazones was also investigated and showed the same dependence on the bulk of the aliphatic group.

THE solvolysis of the hydrazonyl halides (1) in aqueous organic solvents leads to the hydrazides (7). Further hydrolysis of the hydrazide can be minimised and the conversion is essentially quantitative.[1] The hydrazonyl

$$\underset{(1)}{R^1CX{=}N{-}NHR^2} \xrightarrow{H_2O} \underset{(7)}{R^1CONHNHR^2}$$

(2) $X = H, R^2 = 4\text{-}NO_2{\cdot}C_6H_4$
(3) $X = Br, R^2 = 4\text{-}NO_2{\cdot}C_6H_4$
(4) $X = H, R^2 = 2,4\text{-}(NO_2)_2C_6H_3$
(5) $X = Br, R^2 = 2,4\text{-}(NO_2)_2C_6H_3$
(6) $X = Br, R^2 = 2\text{-}Br,4\text{-}NO_2{\cdot}C_6H_3$

bromides (1; X = Br) were chosen as standard substrates to study the mechanistic details of this conversion since (*a*) bromide ion is a sufficiently good leaving group that the rates of solvolysis are within measurable range and (*b*) they are conveniently prepared by direct bromination of the readily obtained hydrazones.

We have previously reported studies on hydrazonyl bromides in which both R^1 and R^2 in (1) were aryl groups.[2] We have now also probed the case where one of these groups (*viz.* R^1) is an aliphatic group. We wished to discover whether the anomalous behaviour shown in the bromination of aliphatic aldehyde 2,4-dinitrophenyl hydrazones (4) was also apparent in the solvolytic behaviour of the corresponding hydrazonyl bromides. The rate-determining step in the bromination of these hydrazones was not bromination itself (as is the case with most other hydrazones) but was attributed to a slow *syn-anti* interconversion in the hydrazone prior to bromination.[3]

TABLE 1

Pseudo first-order rate constants ($10^4k/s^{-1}$) for the hydrolysis of the hydrazonyl bromides (1; X = Br) in dioxan–water (4 : 1)

t/°C	R^2	R^1:	Me	Et	Pr^i	Bu^t	Bu^s	Bu^i	Bu^n	$ClCH_2$	$BrCH_2$	Cl_2CH
25	$4\text{-}NO_2{\cdot}C_6H_4$		1·2	0·7	0·42	0·26	0·44	0·68	0·64			
75	$2,4\text{-}(NO_2)_2C_6H_3$		1·65	1·28	0·99	0·80	1·00	1·18	1·20	5·26	0·38	0·86
50	$2\text{-}Br,4\text{-}NO_2{\cdot}C_6H_3$		1·10	0·75	0·54	0·37	0·54	0·78	0·68			

To establish the standard solvolytic pattern for the aliphatic hydrazonyl halides the *N*-(4-nitrophenyl) derivatives (3) were first investigated. In the bromination of the parent hydrazones (2) with a 1 : 1 bromine : hydrazone ratio, bromination occurred solely at the methine position. The hydrazonyl bromides thus synthesised included those with R^1 = Me, Et, Pr^i, Bu^t, Bu^s, Bu^i, Bu^n, and trifluoromethyl. Although it would have been informative to have available a range of electron-withdrawing substituted compounds to complement the electron-donating alkyl substituents, synthetic difficulties prevented this. Both α- and β-halogenoaldehyde hydrazones on formation underwent further rapid reaction (to give ene-azo-compounds and pyrazolines respectively).[4] In the present series, therefore, only one compound carried an electron-withdrawing (relative to Me) substituent, namely trifluoro-*N*-(4-nitrophenyl)acetohydrazonyl bromide. Presumably the strong C–F bond therein reduced any tendency to undergo elimination.

Solvolysis of the hydrazonyl bromides (3) in 80% dioxan–water gave the corresponding hydrazides (7) in high (78—88%) yield. The kinetics of solvolysis were studied in this solvent by estimating the amount of bromide ion released at various time intervals by titration, using the Volhard technique. The rate constants quoted in Table 1 were obtained by extrapolation of the calculated rate constants to zero per cent reacted (see Experimental section).

From the rate constants listed in Table 1 it is clear that the rate of solvolysis decreases with increasing alkyl substitution of the group R^1. Thus when R^1 = Me the rate of solvolysis is 4·6 times faster than when R^1 = Bu^t (with $R^2 = 4\text{-}NO_2{\cdot}C_6H_4$). This result is unexpected if the alkyl groups exert merely an electronic effect since it implies that the solvolysis is retarded by the more electron-donating t-butyl group.

This arises because in all the substituents increasing bulk is paralleled by increasing electron-donation power. Studies on the trifluoroacetohydrazonyl bromide (3;

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[1] J. B. Aylward and F. L. Scott, *J. Chem. Soc.* (*B*), 1969, 1080.

[2] F. L. Scott, M. Cashman, and A. F. Hegarty, *J. Chem. Soc.* (*B*), 1971, 1607.

[3] A. F. Hegarty and F. L. Scott, *J. Org. Chem.*, 1968, **33**, 753.

[4] F. D. Chattaway and C. H. Farinholt, *J. Chem. Soc.*, 1930, 94.

$R^1 = CF_3$) showed that this compound was hydrolysed very slowly. Even at 75° in 80% dioxan, hydrolysis was far slower (k *ca.* 10^{-7} s^{-1}) than hydrolysis of the corresponding acetohydrazonyl bromide (3; $R^1 = Me$) in the same solvent at 25°. Although the trifluoromethyl and methyl groups vary in bulk ($E_s = 0$ and $-1{\cdot}16$ respectively),[5] it is clear that the large deactivation brought about by the trifluoromethyl group is largely electronic. The Taft σ^* value [5] for the CF_3 group (relative to Me) is $+2{\cdot}8$; unlike the case when alkyl groups alone are concerned, this enormous difference results in electronic effects being of over-riding importance.

No other such compound with electron-withdrawing substituents was available (see before). This difficulty was overcome by using the *N*-(2,4-dinitrophenyl)-alkanohydrazonyl bromides (5). These were synthesised by virtue of the high insolubility of the hydrazones (4); precipitation of the hydrazone occurred before further reaction.

Solvolyses of compounds (5) were carried out in 80% dioxan [at 75° because of the overall reduced reactivity relative to the 4-nitrophenyl series (3)]. The rate constants are summarised in Table 1. It is clear that electron-withdrawal by substituents in R^1 causes a marked decrease in reactivity. Inclusion of all the data in Table 1 for compounds (5) would therefore give a wide scatter if $\log k$ were plotted against σ^* or E_s alone. Use of the full Taft equation [5] however allows these data to be correlated with some precision. (The values of ρ^* and δ are $-0{\cdot}5$ and $+0{\cdot}21$ respectively.)

The data for $R^1 = CHCl_2$ were not included in this correlation since hydrolysis resulted in the release of 2 mol. equiv. of hydrogen halide. The constant quoted in Table 1 was calculated from an initial rate value and a theoretical infinity. Since the observed rate constant obtained thus is far larger than that calculated (with ρ^* and δ given above), an alternate mechanism (possibly involving hydrolysis of the terminal $CHCl_2$ groups) must be operative for this compound. Thus the alkyl groups simultaneously act upon the rate of reaction in two ways: (*a*) electron donation to the reaction centre which aids the solvolysis and (*b*) retardation due to the size of the substituent. Of these two effects (*b*) appears to be the more powerful, so that the overall effect in both series (3) and (5) is deactivation by alkyl groups. Of the possible explanations for the rate retardation by bulky groups perhaps the most plausible is that these substituents inhibit solvation of the carbonium ion formed. Note that the rate of solvolysis is very sensitive to the ionizing power of the medium (*vide infra*).

A third series of compounds, the *N*-(2-bromo-4-nitrophenyl)alkanohydrazonyl bromides (6), was also studied. These compounds were obtained by the dibromination of the hydrazones (2). The position of the second bromine was established by an independent synthesis of the acetohydrazonyl bromide (6; $R^1 = Me$) from 2-bromo-4-nitrophenylhydrazine. The rates of solvolysis of the *N*-(2-bromo-4-nitrophenyl) series (6) were intermediate between the 4-nitrophenyl (3) and 2,4-dinitrophenyl (5) series and were consequently studied in 80% dioxan at 50° (Table 1). The same substituents as for the *N*-(4-nitrophenyl) series (3) were used, the restrictions on available R^1 groups being the same as for the latter series. A detailed four-parameter Taft correlation was therefore not possible.

If it is assumed that the steric effects of substituents R^1 remain the same in the three series of compounds studied, then the susceptibility constant (δ) of $+0{\cdot}21$ obtained for the series (5) can be applied also the other two series. Then, from equation (1), the true electronic

$$\log k/k_0 - 0{\cdot}21E_s = \rho^*\sigma^* \qquad (1)$$

sensitivity factors, ρ^*, can be estimated as $-0{\cdot}35$ and $-0{\cdot}42$ for the other two series (3) and (6). It thus appears that as the ability of the *N*-aryl ring to stabilize positive charge is enhanced [in the order $2,4\text{-}(NO_2)_2C_6H_3 < 2Br,4\text{-}NO_2{\cdot}C_6H_3 < 4\text{-}NO_2{\cdot}C_6H_4$]; changing R^1 has a relatively smaller effect. Similar observations has been noted in the bromination of 1,1-diarylethylenes and the solvolysis of diphenylmethyl chlorides.[6,7] The value of ρ obtained for the variation of substituents was very much dependent on the substituent already present (*e.g.*, a variation in ρ from $-2{\cdot}2$ to $-4{\cdot}2$ was noted for the variation of a second substituent when the first substituent was 4-methoxy- and 4-nitro-, respectively).[6] Other examples of this effect, which results in non-additivity of the substituent constants, have also been noted.[8]

The solvolysis of *N*-(4-nitrophenyl)valerohydrazonyl bromide (3; $R^1 = Bu^n$), chosen as standard, was briefly investigated further; Table 2 summarises the results obtained. It is seen that an equimolar concentration of a salt which does not react with substrate increases the rate of solvolysis markedly. The presence of acid

TABLE 2

Effect of variation of solvent composition and added salts on the rate constants for the hydrolysis of hydrazonyl bromides

Substrate	t/°C	Solvent dioxan–water	[Salt]/M	$10^4k/s^{-1}$
(3; $R^1 = Bu^t$)	25	85 : 15		0·08
		80 : 20		0·26
		75 : 25		0·79
		70 : 30		1·80
(3; $R^1 = Bu^n$)	25	80 : 20	NaBr,10^{-2}	0·32
		80 : 20	H_2SO_4,10^{-2}	6·56
		80 : 20	$NaNO_3$,10^{-2}	4·02
(6; $R^1 = Bu^t$)	50	85 : 15		0·13
		80 : 20		0·37
		75 : 25		1·51
		70 : 30		2·18

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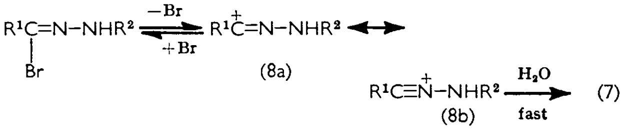
[5] R. W. Taft, jun., 'Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, p. 598.

[6] E. D. Bergman, J. E. Dubois, and A. F. Hegarty, *Chem. Comm.*, 1968, 1616.

[7] S. Nishida, *J. Org. Chem.*, 1967, **32**, 2692, 2695, 2697.

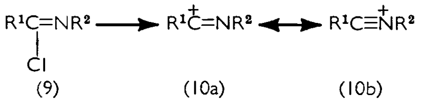
[8] M. M. Bursey and C. E. Twine, *J. Org. Chem.*, 1970, **35**, 2012; J. Hine, 'Physical Organic Chemistry,' McGraw-Hill, 1962, p. 100.

brings about a similar rate increase, most probably for the same reason of increasing the ionizing power of the solvent. The marked effect of the solvent was also evident in the large rate changes brought about by changing the dioxan : water ratios. From the data in Table 2, *m* values of 0·99 and 0·85 [for (3) and (6), $R^1 = Bu^t$] were calculated using the *Y* values for dioxan–water given by Fainberg and Winstein.[9] The degree of positive charge developed in the transition state is therefore close to that in the transition state of the standard reaction for the *mY* solvent treatment (where $m = +1·0$), namely the solvolysis of t-butyl chloride. Further support for a simple ionization mechanism [formation of an azo-carbonium ion (8) (Scheme 1)] is provided by salt effect data in Table 2, where it is seen that although inert salts increase the rate of solvolysis 5—10-fold, a salt with a common ion (NaBr) causes an overall rate depression. When allowance is made for the rate enhancement expected by the presence of the salt simply acting to increase the ionizing power of the solvent, the common ion is seen to have a substantial effect on rate, *viz.* causing a 10—20-fold rate depression. This specific effect is strong evidence for an ionization mechanism with the existence of an intermediate sufficiently long lived to discriminate between the various nucleophiles present in solution.[10]

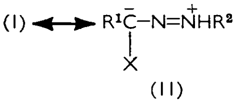


Scheme 1

The results reported by Ugi, Beck, and Fetzer[11] for the solvolysis of the imidoyl chlorides (9) in 66·7% acetone closely parallel those of the present study, *e.g.* initial pseudo-unimolecular constants were used since the apparent rate constants decreased with time. This is best attributed, as in the case of the hydrazonyl bromides (1; X = Br), to the existence of a large common-ion effect. Substituents effects *m*- or *p*- in the aromatic rings R^1 or R^2 in (9) are consistent with the build-up of considerable positive charge in the transition state. However, as in the present instance, steric effects of substituents (R^1) attached to carbon are also of importance, increasing bulk causing decreased reactivity, paralleling the results we have obtained for the solvolysis of the correspondingly substituted *N*-(4-nitrophenyl)alkanohydrazonyl bromides.



Although the solvolyses of imidoyl and hydrazonyl halides were not carried out under directly comparable conditions, the reactivity of one *vis-à-vis* the other can be estimated. The rate of hydrolysis of the benzimidoyl chloride (9; $R^1 = Ph$, $R^2 = 4\text{-}NO_2{\cdot}C_6H_4$) at −20° is $1{\cdot}8 \times 10^{-5}\ s^{-1}$ in 66·7% acetone; at 25° the hydrazonyl bromide (3; $R = Bu^t$) has a corresponding constant of $1{\cdot}8 \times 10^{-4}\ s^{-1}$ in 70% dioxan (a solvent with similar *Y* value). Thus although the solvolytic temperature for (3) is 45° higher, the rate constant is larger only by a factor of 10. This may appear surprising *a priori* since (3) has the better leaving group (Br^- *vs.* Cl^-) and the intermediate (8) has the possibility of extra stabilization through the NH group. The greater reactivity of imidoyl halides is best explained therefore in terms of extra ground-state stabilization of the hydrazonyl halide, possibly through the contribution of structures such as



(11)

$$(1) \longleftrightarrow R^1\overset{-}{C}(X)\text{–}N\text{=}\overset{+}{N}HR^2$$

(11; X = Br). The existence of such 'enamine character' in hydrazones (1; X = H)[12] and 2-pyrazolines[13] has been amply demonstrated.

An alternate mode of reaction, dehydrohalogenation to give 1,3-dipolar ion intermediates $R^1\overset{+}{C}\text{=}N\text{–}\overset{-}{N}R^2$ (12), is available only for hydrazonyl and not for imidoyl halides. This reaction is base catalysed so that in alkaline solution hydrazonyl halides undergo very ready solvolysis.[14] Under the conditions used in the present study in unbuffered solution, the contribution of this pathway is negligible; in any event the HBr generated during solvolysis ensures that the azocarbonium ion pathway alone operates. This has been confirmed in studies on the variation of the rate of solvolysis with the basicity of the medium.[15]

Alkylformazan Formation.—An attempt was made to measure the rates of bromination of the aliphatic aldehyde 4-nitrophenylhydrazones (2) in 70% acetic acid at 20° to compare the charge distribution with that found in the solvolysis of (3). It was also hoped to clarify whether the anomalous kinetic behaviour of alkylidene-2,4-dinitrophenylhydrazines (which were brominated with a kinetic form which was zeroth order in bromine[3]) was common to all aliphatic aldehyde hydrazones. However, the compounds (3) were too reactive towards bromine for reliable rate measurements to be made by the electrometric technique (*i.e.* $k > 10^6$ l mol s^{-1}).

Benzenediazonium ion, on the other hand, is a considerably less powerful electrophile and its reaction with these hydrazones was within measurable range. The solvent used was t-butyl alcohol–water (2 : 3; 20°),

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[9] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.*, 1956, **78**, 2770.

[10] L. C. Bateman, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 1940, 960.

[11] I. Ugi, F. Beck, and U. Fetzer, *Ber.*, 1962, **95**, 126

[12] A. F. Hegarty and F. L. Scott, *J. Chem. Soc.* (*B*), 1966, 672.

[13] P. Bouchet, J. Elguero, and R. Jacquier, *Bull. Soc. chim. France*, 1967, 4716.

[14] A. F. Hegarty, M. Cashman, and F. L. Scott, *Chem. Comm.*, 1971, 680.

[15] A. F. Hegarty, M. Cashman, and F. L. Scott, *J.C.S. Perkin II*, 1972, 44.

buffered at pH 7. The final product of the coupling reaction was the formazan (14), but a recent study[16] has shown that initially attack by the diazonium ion occurs at carbon to give the bis(arylazo)methane (13). Tautomerism of the latter then affords the formazan. In the present study alkylidene-4-nitrophenylhydrazines (2) were used as substrates; isomerization of the intermediates (13) apparently occurred rapidly in this case so that attempts to stop the reaction at this stage were unsuccessful: the formazan (14) was the sole product isolated.

$$(2) + \mathrm{PhN_2^+} \longrightarrow [\mathrm{R^2\overset{+}{N}H{=}N{-}CHR^1{-}N{=}NPh}] \longrightarrow$$

$$\underset{(13)}{[\mathrm{R^2N{=}N{-}CHR^1{-}N{=}NPh}]} \longrightarrow \underset{(14)}{\mathrm{R^2NH{-}N{=}CR^1{-}N{=}NPh}}$$

In fact, precipitation of the more insoluble formazans occurred during a kinetic run. This precipitation did not interfere however with the reaction rate measurements. The rate of disappearance of benzenediazonium ion was followed polarographically, its concentration being proportional to the diffusion current at a dropping-mercury electrode.[17] Since the benzenediazonium ion was the only species reduced when a polarizing voltage of 0·4 V was used, the differing amounts of bis(arylazo)-methane and formazan which were formed as the reaction progressed did not interfere with the rate measurements.

The formazans (14) were also prepared by the reaction of hydrazonyl bromides (3) with phenylhydrazine,[18] and were identical with those obtained from the coupling reaction above. Before recrystallization, however, the characteristics of the compounds isolated by the two methods were quite distinct, possibly because of the presence of different isomeric forms (about C=N and N=N double bonds) of the formazans.[19]

The rate data obtained for the reaction of alkylidene-4-nitrophenylhydrazines with benzenediazonium ion are presented in Table 3. In each case the reaction was overall second order, first order in both hydrazone and diazonium ion. The observed second-order rate constants listed in Table 3 represent the mean of several values obtained at varying initial concentrations of the substrates. The fact that the rate-determining step is the attack of the electrophile rather than a pre-equilibrium (as in the case of aliphatic dinitrophenylhydrazones) could be due to the vast difference in overall reactivity of the electrophiles: the second-order rate constant is *ca.* 10^6 times larger for bromination. Given this large rate difference, it is possible that the slower reaction of diazonium ion permits internal equilibration among the structural isomers of the hydrazone.

TABLE 3

Rate constants for reaction of benzenediazonium ion with alkylidene-4-nitrophenylhydrazines (2) at pH 7 in 40% t-butyl alcohol at 20 °C

R^1	Me	Et	Pr^n	Pr^i	Bu^n
k/l mol^{-1} s^{-1}	4·88	4·32	4·36	3·70	4·09
R^1	Bu^i	Bu^s	Bu^t	Ph_2CH	
k/l mol^{-1} s^{-1}	4·13	3·63	2·95	12·97	

The interpretation of the data for structural variation is limited, however, by the range of hydrazones available for study. In addition to the difficulties inherent in their synthesis, appropriate hydrazones with electron-withdrawing substituents [*e.g.* (4; $R^1 = ClCH_2$)] reacted so slowly with diazonium ion that solvolytic decomposition of the diazonium ion masked the coupling reaction. However, from the limited data in Table 3, it is seen that the rate constants do in fact parallel those obtained for the solvolysis of the corresponding hydrazonyl bromides; thus the rate of reaction decreases with increasing alkyl substitution in much the same way. This relationship between electrophilic attack on hydrazones and solvolysis of hydrazonyl bromides has been noted before[2] in related systems resulting from the intervention of similar charged species (8) and (12) in both reactions.

EXPERIMENTAL

Materials.—All inorganic chemicals used were AnalaR grade; sodium bromide, sodium nitrate, anhydrous sodium acetate, potassium nitrate, and potassium dihydrogen phosphate were dried at 120° for 3 h before use and borax was twice crystallised from water and air-dried to constant weight. Dioxan (BDH AnalaR) was used without further purification; water had been passed through a mixed cation–anion exchange resin and then twice distilled from alkaline potassium permanganate, while t-butyl alcohol (reagent grade) was heated under reflux over sodium (3 g per 1000 ml) and distilled, the fraction with b.p. 82—82·5° was then used. All solvent mixtures were prepared at 25° and are by volume. The 40% t-butyl alcohol mixture was prepared as previously described.[16] Aniline (AnalaR) was distilled from zinc dust and then *in vacuo*; the product had b.p. 85° at 20 mmHg. The aldehydes were commercially available; liquid aldehydes were distilled before use.

All of the compounds prepared had satisfactory analyses, the data are tabulated in Supplementary Publication No. SUP 20424 (8 pp., 1 microfiche).*

N-(4-*Nitrophenyl*)*alkanohydrazonyl Bromides.*—The alkylidene-4-nitrophenylhydrazines were prepared by standard methods using equimolar amounts of 4-nitrophenylhydrazine and the aldehyde in ethanol The m.p.s were in agreement with literature values.[20] Trifluoroacetaldehyde 4-nitrophenylhydrazone was prepared by dissolving 4-

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10pp. are supplied as full size copies).

[16] A. F. Hegarty and F. L. Scott, *J. Org. Chem.*, 1967, **32**, 1957.

[17] R. M. Elofson, R. L. Edsberg, and P. A. Mechesly, *J. Electrochem. Soc.*, 1950, **97**, 166; R. M. Elofson, *Canad. J. Chem.*, 1958, **36**, 1207.

[18] H. von Pechmann, *Ber.*, 1894, **27**, 320; F. D. Chattaway and A. J. Walker, *J. Chem. Soc.*, 1925, 975; A. F. Hegarty and F. L. Scott, *J. Chem. Soc.* (*C*), 1967, 2507.

[19] G. R. Burns and J. F. Duncan, *Chem. Comm.*, 1966, 116.

[20] C. D. Hodgman, 'Tables for Identification of Organic Compounds,' Chemical Rubber Publishing Co., Ohio, 1960, pp. 68—80.

nitrophenylhydrazine (380 mg, 2·5 mmol) in water (10 ml) containing concentrated hydrochloric acid (*d* 1·18, 0·2 ml). Trifluoroacetaldehyde (0·4 ml, 5 mmol) was added and the solution was heated at 40° for 5 min; it was then kept at room temperature for 1 h, during which time *trifluoroacetaldehyde 4-nitrophenylhydrazone* separated as fine yellow needles (520 mg, 90%), m.p. 210—212° (from ethanol–water) (Found: C, 41·0; H, 2·7; N, 17·8. $C_8H_6F_3N_3O_2$ requires C, 41·2; H, 2·6; H, 18·0%). Attempts to prepare the chloro- or bromo-acetaldehyde 4-nitrophenylhydrazone by either of the methods outlined above were unsuccessful; black oils, presumably resulting from cyclization of the hydrazones, and some unchanged starting materials being isolated.

The *N*-(4-nitrophenyl)alkanohydrazonyl bromides were obtained by bromination with hydrazone–bromine (1 : 1) at 0 °C. A 5-fold excess of bromine led to the *N*-(2-bromo-4-nitrophenyl)alkanohydrazonyl bromides.

N-(4-*Nitrophenyl*)*acetohydrazonyl Bromide*.—Acetaldehyde 4-nitrophenylhydrazone (0·5 g, 3 mmol) was suspended in glacial acetic acid (4 ml) containing 5% acetic anhydride in an ice-bath and stirred vigorously. Bromine (0·15 ml, 3 mmol) was added, and the hydrazone dissolved; the hydrazonyl bromide precipitated after a further 1 min, and was washed with light petroleum (b.p. 40—60°) and recrystallised from glacial acetic acid, m.p. 126°.

The other hydrazonyl bromides (3) were prepared in a similar manner: R^1 = Et, m.p. 103°; $\mathrm{Pr^i}$, 93°; $\mathrm{Bu^t}$, 112°; $\mathrm{Bu^s}$, 67°; $\mathrm{Bu^i}$, 79°; $\mathrm{Bu^n}$, 78°; CF_3, 166°.

N-(2-*Bromo*-4-*nitrophenyl*)*acetohydrazonyl Bromide*.—(*a*) Acetaldehyde 4-nitrophenylhydrazone (0·5 g, 3 mmol) was stirred in glacial acetic acid (4 ml) and bromine (0·72 ml, 15 mmol) was added dropwise during 5 min. The hydrazone dissolved and after a further 5 min the hydrazonyl bromide (0·70 g, 80%) precipitated, m.p. 150° (from glacial acetic acid). The other members of the series (6) were prepared (in 65—80% yield) in a similar manner: R^1 = Et, m.p. 86°; $\mathrm{Pr^i}$, 66°; $\mathrm{Bu^t}$, 117°; $\mathrm{Bu^s}$, 49°; $\mathrm{Bu^i}$, 51°; $\mathrm{Bu^n}$, 63°.

(*b*) 2-Bromo-4-nitrophenylhydrazine (prepared by the method of Chattaway [21]) (0·5 g) was dissolved in alcohol (15 ml) and acetaldehyde (0·5 ml) added neat. The solution was heated at 50° for 5 min and on cooling acetaldehyde 2-bromo-4-nitrophenylhydrazone precipitated. The hydrazone (0·5 g) was suspended in glacial acetic acid and stirred vigorously while bromine (0·5 ml) was added. After stirring for 30 min, the product was identical with *N*-(2-bromo-4-nitrophenyl)acetohydrazonyl bromide prepared in (*a*). This hydrazonyl bromide was also prepared by bromination (with 1 equiv. of bromine in acetic acid) of *N*-(4-nitrophenyl)acetohydrazonyl bromide.

N-(2,4-*Dinitrophenyl*)*alkanohydrazonyl Bromides*.—The alkylidene 2,4-dinitrophenylhydrazones were prepared by standard procedures and had m.p.s consistent with literature [20] values. The bromo-, chloro-, dichloro-, and trichloro-acetaldehyde derivatives were prepared by the method of Ross and Ring.[22]

Acetaldehyde 2,4-dinitrophenylhydrazone (3 g, 10 mmol) was suspended in glacial acetic acid (8 ml) containing 2% acetic anhydride, and vigorously stirred while bromine (3 ml) in acetic acid (2 ml) was added rapidly. The hydrazone immediately dissolved to give a deep red solution and the *N*-(2,4-dinitrophenyl)acetohydrazonyl bromide precipitated in 85% yield after 2 min. It was washed with light petroleum (b.p. 40—60°) and crystallised from glacial acetic acid. The other *N*-(2,4-dinitrophenyl)hydrazonyl bromides (5) were prepared (in 60—90% yield) in a similar manner ; the less reactive hydrazones remained in solution for up to 10 min: R^1 = Me, m.p. 148°; Et, 114°; $\mathrm{Pr^i}$, 117°; $\mathrm{Bu^t}$, 155°; $\mathrm{Bu^s}$, 103°; $\mathrm{Bu^i}$, 93°; $\mathrm{Bu^n}$, 94°; $ClCH_2$, 145°; $BrCH_2$, 158°. In all cases, the hydrazonyl bromide rather than the *N*-bromohydrazone structure was indicated since (*a*) i.r. spectra showed a sharp N–H stretching band at 3·0 μm and (*b*) the compounds did not oxidize iodide ion in acidic solution. The structure was also confirmed by the ready conversion into hydrazides (see later).

Kinetic Measurements

(a) *Solvolytical Studies*.—The kinetics of solvolysis of the hydrazonyl bromides (5) were studied in dioxan–water (4 : 1) at 75·0 ± 0·4°, compounds (6) at 50·0 ± 0·4°, and compounds (3) at 25·0 ± 0·4°. Karl–Fischer titration showed the solvent to be within ±0·5% of the desired composition. The reactions at 50 or 75° were carried out in sealed-glass ampoules. At 25°, stoppered volumetric flasks were used.

Rate constants (*k*), which were calculated from the first order equation (2), decreased during the runs; the *k* values

$$k = 2\cdot303t^{-1}\log\,[a/(a - x)] \qquad (2)$$

reported were calculated by extrapolating the plot of *k vs.* % reaction to 0% reaction. The rate constants quoted are average values obtained from at least three separate experiments.

(b) *Reactions with Benzenediazonium Ion*.—The kinetics of the reaction between benzenediazonium ion and hydrazones were measured polarographically; the experimental details have been described previously.[17] Most of the runs were followed to 80% completion. Individual rate constants were estimated to be accurate to ±5% and the values quoted are the mean of 3—6 runs.

Product Analysis.—(a) *Hydrazides*. The solvolysis of hydrazonyl bromides in aqueous dioxan was found to give a quantitative yield of the corresponding hydrazides. These solvolyses were carried out in 50% dioxan–water to speed up the reaction; repetition of the solvolyses under rate conditions was found not to affect the yield of the solvolysis product, the only difference being that the reactions had to be run for much longer times.

Solvolysis of N-(2,4-*dinitrophenyl*)*acetohydrazonyl bromide*. *N*-(2,4-Dinitrophenyl)acetohydrazonyl bromide (1·0 g, 3·3 mmol) was dissolved in dioxan–water (1 : 1, 100 ml) and heated under reflux for 2 h. On cooling, *N*-(2,4-dinitrophenyl)acetohydrazide (296 mg, 37%) precipitated, m.p. 199°. Addition of water (75 ml) precipitated a further quantity (400 mg, 50%) of the hydrazide, m.p. 195—198°. The filtrate was extracted with ether; the dried (Na_2SO_4) extracts, on evaporation, gave a further quantity of the crude hydrazide (24 mg, 3%), m.p. 190—195°.

The other members of this series were treated in a similar manner. The *N*-(2-bromo-4-nitrophenyl)- and *N*-(4-nitrophenyl)-alkanohydrazonyl bromides were also treated similarly except that the reflux times were shorter: 90 min for the *N*-(2-bromo-4-nitrophenyl) series and 60 min for the *N*-(4-nitrophenyl) series. The hydrazides (6) had the following m.p.s: R^2 = $4\text{-}NO_2\cdot C_6H_4$; R^1 = Me, 214°; Et, 205°; $\mathrm{Pr^i}$, 185°; $\mathrm{Bu^t}$, 112°; $\mathrm{Bu^s}$, 167°; $\mathrm{Bu^i}$, 139°;

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[21] F. D. Chattaway and A. J. Walker, *J. Chem. Soc.*, 1925, 975.

[22] A. Ross and R. N. Ring, *J. Org. Chem.*, 1961, **26**, 579.

Bu^n, 142°. R^2 = 2-Br,4-NO_2·C_6H_3, R^1 = Me, 172°; Et, 169°; Pr^i, 182°; Bu^t, 145°; Bu^s, 155°; Bu^i, 136°; Bu^n, 110° and R^2 = 2,4-$(NO_2)_2C_6H_3$, R^1 = Me, 199°; Et, 184°; Pr^i, 205°; Bu^t, 185°; Bu^s, 178°; Bu^i, 147°; Bu^n, 127°. The i.r. spectra of these hydrazides all showed bands at 6·0 (C=O) and 3·02 µm (N–H). The aqueous layer (from the ether extraction) was titrated for bromide ion (Volhard); the theoretical amount ±2% (*i.e.* 10 mmol) was present in all cases. Several hydrazides (at least one from each series) were also prepared unambiguously by reaction of the acid chloride with the appropriate hydrazine in dry pyridine. The products obtained were identical with those resulting from solvolysis of the hydrazonyl bromides.

(*b*) *Formazans.* The amount of product actually formed during a kinetic experiment involving the coupling of benzenediazonium ion and the 4-nitrophenylhydrazones was so small that these experiments had to be repeated on a larger scale to permit product isolation. The following describes the typical procedure. The hydrazone (0·01 mol), while stirred in ethanol (100 ml) at 0 °C, was treated with benzenediazonium acetate [prepared by the diazotization of anline (0·93 g, 0·01 mol) in 3M-hydrochloric acid (10 ml, 0·03 mol) with sodium nitrite (0·76 g, 11 mmol) in water (2 ml) at 0°] and anhydrous sodium acetate (1·64 g, 0·02 mol) was then added. The deep red formazan which slowly separated from the enthanolic diazonium ion plus hydrazone solution was filtered off (after 60 min) and thoroughly washed with ice–water and with pentane (3—4 recrystallisations were necessary to obtain a material with constant m.p.). The 5-(4-nitrophenyl)-1-phenylformazans (14; R^2 = 4-NO_2·C_6H_4) had following m.p.s: 3-methyl, 155—156°; 3-ethyl 158°; 3-n-propyl, 154°; 3-isopropyl, 176—177°; 3-n-butyl, 138°; 3-isobutyl, 169°; 3-s-butyl, 154°; 3-t-butyl, 126°; 3-diphenylmethyl, 201°.

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