

## Mechanism of Cyclisation of *N*-(1,2,4-Triazol-3-yl)hydrazonyl Bromides to Mixtures of Isomeric Triazolotriazoles

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The reaction of *N*-(5-phenyl-1,2,4-triazol-3-yl)arenohydrazonyl bromides (2) in mixed aqueous, organic solvents may yield three products, dependent on the acidity of the medium. In strongly acidic solution *N*-(5-phenyl-1,2,4-triazol-3-yl)arenohydrazides (4) are formed as major products; at pH 3–6, 3-aryl-5-phenyl-1*H*-s-triazolo-[3,4-*c*]-s-triazoles (5) were formed exclusively while in basic media the isomeric 3-aryl-6-phenyl-5*H*-s-triazolo-[4,3-*b*]-s-triazoles (6) [which are also formed by the action of lead tetra-acetate on the hydrazone (1)] predominate. Kinetic studies (in 85:15 dioxan–water at 25°) indicate that in neutral solution (5) is formed by intramolecular cyclisation of the neutral triazole on an azocarbonium ion centre (Hammett  $\rho$  for the variation of substituents in Ar is  $-1.32$ ); when the triazole ring is protonated intermolecular attack by water [formation of (4) occurs]. The isomer (6) is formed by [1,5] dipolar cycloaddition involving the triazolyl anion as nucleophile. The isomer (6) was synthesised by an independent route. Under appropriate conditions intermolecular reactions of (2) with chloride ion, aniline, and morpholine yielded products in which bromide ion was replaced by the nucleophile.

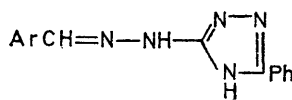
It is well established that alkylation of ambident nucleophiles depends, *inter alia*, on the nature of the alkylating agent (whether, for example, it shows reactivity of the  $S_N1$  or  $S_N2$  type) and on the reactive form of the nucleophile present in solution.<sup>1,2</sup> These principles have also been applied to heterocyclic synthesis,<sup>3</sup> and are particularly useful in predicting the mode of reaction when various possible sites for cyclisation are possible. In this study we describe the synthesis of the novel *N*-triazolylhydrazonyl bromides (2) and report on the competing modes of reaction of (2) (including cyclisation) which occur on solvolysis.

### RESULTS AND DISCUSSION

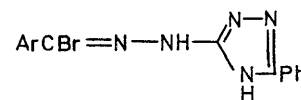
When arylidene-(5-phenyl-1,2,4-triazol-3-yl)hydrazines (1) were treated with an equimolar amount or two-fold excess of bromine in acetic acid, the triazolylhydrazonyl bromide hydrobromides (2, HBr) were formed in good yield. The salts solvolysed very rapidly (see below) but could be converted into hydrazonyl bromide free bases by careful distribution between ether and water. The hydrazonyl bromide structure (2) is consistent with the observed i.r. and u.v. spectra [which are similar to those of the starting hydrazone (1)], and with the ready conversion into the corresponding hydrazide (4) in aqueous acid and into the anilide (3) or morpholide in the presence of aniline or morpholine. Both the latter reactions are typical of hydrazonyl bromides.<sup>4</sup>

On dissolution in aqueous acetone the hydrazonyl bromide hydrobromides (2, HBr) were solvolysed with the release of two equivalents of bromide ion to give a mixture of products. The relative amounts of the

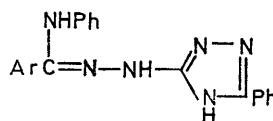
various products depended on the nature of the *C*-aryl (Ar) substituent. The study of these reactions was hampered by the formation of resinous gums when reaction and isolation were carried out at room temperature. In these cases addition of a small volume of



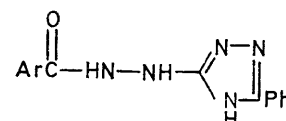
(1)



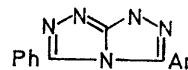
(2)



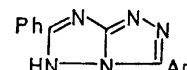
(3)



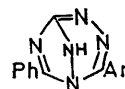
(4)



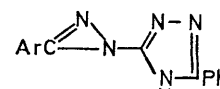
(5)



(6)



(7)



(8)

acetone to the resinous material was usually successful in separating the gum from the crystalline materials. Less decomposition occurred when solvolysis was

<sup>3</sup> See, for example, T. Kappe, P. F. Fritz, and E. Ziegler, *Chem. Ber.*, 1973, **106**, 1927, and previous papers in this series.

<sup>4</sup> A. F. Hegarty, M. P. Cashman, and F. L. Scott, *J.C.S. Perkin II*, 1972, 44.

<sup>1</sup> R. Gompper, *Angew. Chem. Internat. Edn.*, 1964, **3**, 560.

<sup>2</sup> N. Kornblum, R. Seltzer, and P. Haberfield, *J. Amer. Chem. Soc.*, 1963, **85**, 1148 and references cited therein.

carried out at 0°, but even then work-up was usually complicated by varying amounts of intractable materials.

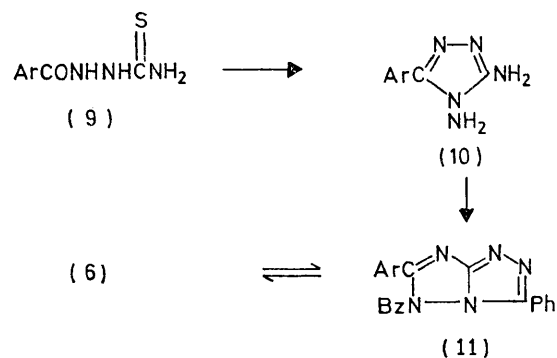
Thus when the hydrazonyl bromide (2, HBr; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>), was dissolved in 80% acetone at 0°, two products were isolated, the hydrazide (4) and the triazolotriazole (5) in 70 and 18% yield respectively. The structure of the hydrazide (4) is consistent with i.r. data; moreover the hydrazide was prepared independently by the reaction of 5-hydrazino-3-phenyl-1,2,4-triazole with the aroyl chloride, giving the identical hydrazide (4).

There are several possible structures for the minor product of solvolysis of (2; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>). Analytical data establish the formula as C<sub>15</sub>H<sub>10</sub>BrN<sub>5</sub>. Each of the four structures (5)–(8) meets this requirement. These arise by ring closure from positions N-4, N-1, N-2, and N-6 respectively. Attack at position N-2 of the triazole ring, although conceivable, is not likely since such a ring closure would result in the formation of a bicyclo[3.2.1] system containing bridgehead unsaturation [see (7)]. In a study of the application of Bredt's rule<sup>5</sup> to bicyclic systems it has been found<sup>6</sup> that [3.3.1] is the minimum bicyclic system which is compatible with unsaturation at the bridgehead, and that this is a highly unstable system. An examination of molecular models indicates that the existence of (7), even as a reactive entity, is unlikely in view of the large strain involved in the puckered rings.

The diazirine structure (8) is also unlikely for a crystalline substance of m.p. 255°. While a considerable amount of work has been carried out on diazirines and diaziridines,<sup>7</sup> no diazocyclopropane containing a C=N bond, as in structure (8) has been reported. Moreover the diazirine is isomeric with a 1,3-dipolar ion [formed from (2) by loss of a mole of HBr] and such a mode of cyclisation of 1,3-dipolar ions has not been reported despite the wide study of such species.<sup>7</sup>

Of the two remaining structures (5) and (6), the N-1 closure product (6) can be eliminated. This was previously isolated from the reaction of *p*-bromobenzylidene-(5-phenyl-1,2,4-triazol-3-yl)hydrazine (1; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>) with lead tetra-acetate (LTA).<sup>8</sup> Compound (6) was also unambiguously synthesised by the sequence outlined in Scheme 1. The 1-aryylthiosemicarbazides (9; Ar = *p*-MeOC<sub>6</sub>H<sub>4</sub>, *p*-MeC<sub>6</sub>H<sub>4</sub>, Ph, or *p*-ClC<sub>6</sub>H<sub>4</sub>) were prepared by stirring powdered thiosemicarbazide with the appropriate aroyl chloride in pyridine at 0°. The reaction of (9) with 50% hydrazine hydrate<sup>6</sup> produced the desired 3,4-diamino-5-aryl-1,2,4-triazoles (10) as well as some 5-aryl-1,2,4-triazole-3-thiols. When this reaction was attempted with Ar = *p*-MeOC<sub>6</sub>H<sub>4</sub>, no diaminotriazole was isolated; instead 5-*p*-methoxyphenyl-1,2,4-triazole-3-thiol was isolated in 68% yield. 3,4-Diamino-5-(*p*-methoxyphenyl)-1,2,4-triazole (10;

Ar = *p*-MeOC<sub>6</sub>H<sub>4</sub>) was prepared however using a modification suggested by Hoggarth,<sup>9</sup> viz. conversion of (9) into the *S*-methyl sulphide followed by reaction with hydrazine hydrate. Support for the diamino-structure for compound (10) is provided by the formation<sup>10</sup> of an *NN'*-dibenzylidene derivative from (10; Ar = Ph) with benzaldehyde and by the ready condensation of (10; Ar = Ph) with  $\alpha$ -diketones such as benzil and diacetyl to give tetrazolo[1,2-*a*]triazines.



SCHEME 1

When the diaminotriazoles (10; Ar = *p*-MeOC<sub>6</sub>H<sub>4</sub>, *p*-MeC<sub>6</sub>H<sub>4</sub>, Ph, or *p*-ClC<sub>6</sub>H<sub>4</sub>) were treated with an excess of benzoyl chloride in pyridine, the monobenzoyl derivatives of the 3-aryl-6-phenyl-5H-s-triazolo[4,3-*b*]-s-triazoles (11) were formed. Hydrolysis in concentrated hydrochloric acid effected debenzoylation to give the triazolotriazoles (6). These materials (6; Ar = *p*-MeOC<sub>6</sub>H<sub>4</sub>, *p*-MeC<sub>6</sub>H<sub>4</sub>, Ph, and *p*-ClC<sub>6</sub>H<sub>4</sub>) were identical (i.r. and u.v. spectra, mixed m.p.s) with the materials obtained on treatment of the corresponding hydrazones (1) with lead tetra-acetate;<sup>8</sup> the same tests however showed that the material obtained on cyclisation of the hydrazonyl bromide (2; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>) was not (6; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>). This leaves (5; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>), the material resulting from attack by the N-4 position of the triazole ring, as the most likely structure of the minor solvolytic product formed from the hydrazonyl bromide (2; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>).

When the hydrobromide of the *p*-chlorophenyl compound (2, HBr; Ar = *p*-ClC<sub>6</sub>H<sub>4</sub>) was solvolysed, the hydrazide (4; Ar = *p*-ClC<sub>6</sub>H<sub>4</sub>) was isolated in 57% yield; extensive decomposition had also occurred and no triazolotriazole could be isolated from the resinous gum formed.

Solvolysis in the presence of base, but again at low temperature and followed by careful work-up, gave higher yields of the cyclic materials (5) and (6); under these conditions also, no hydrazide was formed. When (2, HBr; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>) was treated at 0° in 4:1 acetone-water in the presence of two equivalents of sodium carbonate, (5; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>) was isolated in

<sup>5</sup> F. A. Fawcett, *Chem. Rev.*, 1950, **47**, 219.

<sup>6</sup> J. R. Wiseman, *J. Amer. Chem. Soc.*, 1967, **89**, 5966; J. A. Marshall and H. Faubl, *ibid.*, p. 5965; J. P. Schaefer, J. C. Lark, C. A. Flegal, and L. M. Honig, *J. Org. Chem.*, 1967, **32**, 1372; P. von Schleyer, E. Funke, and S. H. Liggers, *J. Amer. Chem. Soc.*, 1969, **91**, 3965.

<sup>7</sup> R. A. Reed, *Chem. and Ind.*, 1966, 529.

<sup>8</sup> F. L. Scott and T. A. F. O'Mahony, *Tetrahedron Letters*, 1970, 1841; see also J. D. Bower and F. P. Doyle, *J. Chem. Soc.*, 1957, 727.

<sup>9</sup> E. Hoggarth, *J. Chem. Soc.*, 1950, 1579.

<sup>10</sup> E. Hoggarth, *J. Chem. Soc.*, 1950, 614.

75% yield, together with a small amount of the isomeric (6; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>) (2%). In the presence of sodium hydroxide (two equivalents) the same hydrazonyl bromide gave more decomposition, but of the crystalline products isolated, the N-1 attack product (6) predominated [36% vs. 11.5% of (5)]. It thus appears that (a) in basic or mildly basic solution hydrazide formation of (4) is suppressed and (b) in mildly basic solution (5) is the predominant product while at higher pH (6) is formed in greater yield.

In the absence of base, solvolysis of the phenyl compound (2, HBr; Ar = Ph) yielded only a resinous gum. In the presence of two equivalents of sodium acetate, however, (5; Ar = Ph) was isolated in 67% yield. This material was isomeric (by analysis and molecular weight) with (6; Ar = Ph) which itself was isolated from the LTA oxidation of the corresponding hydrazone (1; Ar = Ph) and also synthesised independently (Scheme 2). Both materials also had the same m.p. (266°), but depressed *ca.* 20° when mixed; their i.r. and u.v. spectra were also different.

We have also found t.l.c. on silica gel useful in the identification and separation of (4)–(6). For example (5 and 6; Ar = Ph) had *R<sub>F</sub>* values of 0.57 and 0.21 respectively using ethyl acetate–chloroform–methanol (6:6:1) as eluant. However, the hydrazonyl bromides (2) cyclise spontaneously to mixtures of (5) and (6) on the t.l.c. plate; it was therefore essential to ensure that the reaction of (2) was complete (by *e.g.* bromide ion titration) before t.l.c. analysis of the products was undertaken.

The establishment of the structures of the isomeric triazolotriazoles was also consistent with the u.v. data of Potts and Hirsch,<sup>11</sup> who isolated isomeric mixtures of *s*-triazolo-[4,3-*b*]- and -[3,4-*c*]-*s*-triazoles from the reaction of 3-hydrazino-1,2,4-triazoles with cyanogen bromide in aqueous methanol. These workers observed from an analysis of u.v. spectral data that the [4,3-*b*]-isomers absorbed at shorter wavelengths, but with relatively higher intensities than the corresponding [3,4-*c*]-isomers. Some u.v. data for compounds (5) and (6) are recorded in Table 1. It is apparent that our

TABLE 1

U.v. spectral data for some triazolotriazole derivatives

Substrate	System	$\lambda_{\max.}/\text{nm}^a$	$\log \epsilon_{\max.}$
(6; Ar = Ph)	[4,3- <i>b</i> ]	254	4.27
(5; Ar = Ph)	[3,4- <i>c</i> ]	265	4.12
(6; Ar = <i>p</i> -BrC <sub>6</sub> H <sub>4</sub> )	[4,3- <i>b</i> ]	255	4.31
		276	4.25
(5; Ar = <i>p</i> -BrC <sub>6</sub> H <sub>4</sub> )	[3,4- <i>c</i> ]	227	4.14
		284	4.20

<sup>a</sup> In 95% ethanol.

results are consistent with those of Potts and Hirsch.<sup>11</sup> Both the bathochromic shifts and intensity differences are of the same order of magnitude as those reported. This trend in the u.v. spectral data has also been observed

<sup>11</sup> K. T. Potts and C. Hirsch, *J. Org. Chem.*, 1968, **33**, 143.

<sup>12</sup> A. H. Beckett, R. G. W. Spickett, and S. H. B. Wright, *Tetrahedron*, 1968, **24**, 2839; G. W. Millar and F. L. Rose, *J. Chem. Soc.*, 1963, 5642; N. K. Baser and F. L. Rose, *ibid.*, p. 5660.

with the structurally isomeric triazolo-pyrimidines,<sup>12</sup> -pyridines,<sup>13</sup> and -pyrazines.<sup>14</sup> Of interest also is the report of Potts and Hirsch<sup>11</sup> that the [3,4-*c*]-isomers decompose at the m.p. while the [4,3-*b*]-compounds do not; similar behaviour is shown by compounds (5) and (6) as assigned.

In order to determine the factors influencing the two competing cyclisation modes and hydrazide formation, the kinetics of hydrolysis of the hydrazonyl bromides (2) were investigated (Scheme 2). Because of the rapidity of the solvolytic reactions, 85:15 dioxan–water was used as solvent at 25°; at higher aqueous solvent contents, the reactions were too fast to be followed by conventional techniques. The solvolyses were also sensitive to the acidity of the medium and pH was maintained constant (at  $\mu$  0.05M; NaClO<sub>4</sub>) either with perchloric acid, or at higher pH using a pH-stat. The rates of reaction in most cases are pH-independent in the region pH 3–5 and then rise rapidly as the pH is raised; see Table 2 for a typical *k<sub>obs</sub>*–pH profile [for

TABLE 2

Observed rate constants for the hydrolysis of the hydrazonyl bromide (2; Ar = Ph) in 85:15 dioxan–water ( $\mu$  0.05M) at 25° as a function of the pH of the medium

pH	3.0	3.45	4.0	4.5	5.0	5.45	5.95	6.45
$10^2 k_{\text{obs}}/\text{s}^{-1}$	12.1	12.7	12.3	11.9	13.7	16.9	23.1	34.0

TABLE 3

Summary of observed rate constants for the hydrolysis of the hydrazonyl bromides (2; Ar = XC<sub>6</sub>H<sub>4</sub>) at 25° in 85:15 dioxan–water \* (a) average pH-independent value in pH region 3–5, (b) value at pH 6.0

Substituent	<i>p</i> -Me	<i>p</i> -H	<i>p</i> -Br	<i>m</i> -Br	<i>p</i> -NO <sub>2</sub>
(a) $10^2 k_{\text{obs}}/\text{s}^{-1}$	18	12.2	5.1	3.4	—
(b) $10^2 k_{\text{obs}}/\text{s}^{-1}$	35	25	16	—	23

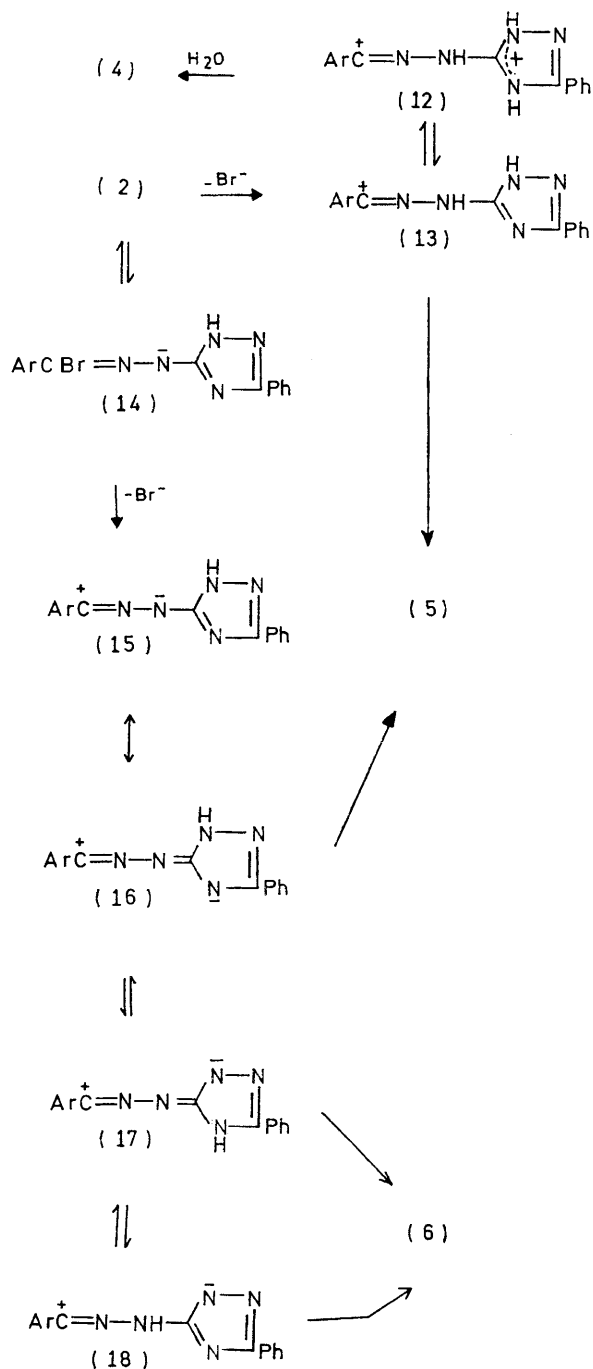
\*  $\mu$  = 0.05M (NaClO<sub>4</sub>).

(2; Ar = Ph)]. In all cases the rate of cyclisation was too rapid to measure at pH 7. In the case of (2; Ar = *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), the pH-dependent rate was dominant over the entire range studied (pH 4.5–6.1); below pH 4.5 the spectral change was too small to permit the measurement of reliable rate constants. Compound (2; Ar = *p*-MeOC<sub>6</sub>H<sub>4</sub>) reacted too rapidly over the entire pH range. In Table 3 are summarised (a) the average pH-independent 'plateau' rate constants obtained from data in the pH region 3–5 and (b) the observed rate constant for the solvolysis of (2) at pH 6 (where the solvolysis is in all cases base catalysed). Separate experiments using either the hydrazonyl bromide hydrobromide salts or the free base (2) gave similar results. By using a higher substrate concentration ( $5 \times 10^{-3}\text{M}$ ) than that used for the kinetic experiments it was shown by Volhard titration that the theoretical quantity  $\pm 2\%$  of bromide ion [two equivalents from (2, HBr) and one from the free base (2)] was released on solvolysis.

<sup>13</sup> M. R. Burton, Ph.D. Thesis, University of Louisville, 1963.

<sup>14</sup> G. M. Badger, P. J. Nelson, and K. T. Potts, *J. Org. Chem.*, 1964, **29**, 2542.

The kinetic results and the products of solvolysis are explicable in terms of the reaction pathways outlined in Scheme 2. In this scheme the substrate (2) gives rise



SCHEME 2

to three products, the hydrazide (4) and the cyclic materials (5) and (6), depending upon the reaction conditions used. It has been well established<sup>14</sup> that hydrazonyl bromides of the type  $\text{R}^1\text{CBr}=\text{N}-\text{NHR}^2$  (16) can be solvolysed in aqueous media by either azocarbenium ion formation (resulting from bromide ion loss from the neutral substrate) or by a base catalysed

process which involves 1,3-dipolar ion formation. The pH-rate profiles shown by compounds (2) are consistent with this behaviour; in the region pH 3–5 (where the observed rate is independent of pH) azocarbenium ion (13) formation is the major reaction pathway. This was confirmed by examining the effect of structure on reactivity; a plot of  $\log k_{\text{obs}}$  vs.  $\sigma$  in this region gave a Hammett  $\rho$  value of  $-1.32$  ( $r$  0.995). The magnitude of the  $\rho$  value is consistent with rate-determining formation of a stabilised carbonium ion species such as (13) and is well within the range of values previously reported for the solvolysis of cognate systems.<sup>15</sup> In this pH region the sole product isolated was the cyclic material (5). This was shown both by comparison of the u.v. spectrum of the final product with that of an authentic sample of compound (5), and by t.l.c. which showed (within the limits of detection) no hydrazide (4) or isomeric triazolotriazole (6) formation. This was confirmed by carrying out the solvolyses on a large scale using either (a) the hydrobromide of (2;  $\text{Ar} = \text{Ph}$  or  $p\text{-BrC}_6\text{H}_4$ ) in aqueous dioxan or acetone in the presence of two equivalents of sodium carbonate or (b) the free base (2;  $\text{Ar} = \text{Ph}$  or  $p\text{-BrC}_6\text{H}_4$ ) in the presence of sodium acetate-acetic acid buffer; up to 75% (5;  $\text{Ar} = p\text{-BrC}_6\text{H}_4$ ) was isolated under these conditions.

In acidic solution (pH < 3) the solvolysis of (2) is very much reduced and kinetic measurements were made more difficult because the spectral change on reaction was small. The change in rate of solvolysis is accompanied by a change in product since in highly acidic solution the hydrazide (4) is the major product formed (up to 70% when  $\text{Ar} = p\text{-BrC}_6\text{H}_4$ ) together with decreasing quantities of (5) (as the acidity of the medium is increased). The change-over corresponds approximately to the pH region where the triazole ring of the substrate is protonated. Because of the reactivity of (2), no direct  $\text{p}K_{\text{a}}$  measurements were possible but an analogue, the hydrazone (1;  $\text{Ar} = p\text{-BrC}_6\text{H}_4$ ), had  $\text{p}K_{\text{a}}$  1.8 (measured spectrophotometrically in 4:1 acetone-water; 25°;  $\mu$  0.1M). Thus in the pH region where (4) is the major product the triazole ring of (2) is substantially protonated inhibiting its action as a neighbouring group. Consequently the carbonium ion centre (12) is scavenged by water yielding (4).

The hydrazide (4) did not result from hydrolysis of the cyclic materials (5) or (6) in acidic solution. Thus when a mixture of (5) and (6) was refluxed for 1 h in 85:15 dioxan-water in the presence of 0.1M-perchloric acid; these were recovered unchanged and t.l.c. analysis indicated no significant hydrazide (4) formation.

When the solvolysis of (2;  $\text{Ar} = p\text{-BrC}_6\text{H}_4$ ) was carried out in 85:15 dioxan-water in the presence of hydrochloric acid (rather than perchloric acid) an interesting halogen interchange took place. The product isolated (after 15 h at room temperature) was the corresponding *N*-(5-phenyl-1,2,4-triazol-3-yl)-*p*-bromobenzohydrazonyl chloride, isolated in 85% yield. This

<sup>15</sup> A. F. Hegarty, J. Cronin, P. A. Cashell, and F. L. Scott, *J.C.S. Perkin II*, 1973, 1708.



is explicable in terms of Cl<sup>-</sup> attack on the azocarbonium ion (13) [or the protonated species (12)]; because of the poorer leaving ability of Cl<sup>-</sup> (relative to bromide ion),<sup>16</sup> the hydrazonyl chloride is relatively stable in acidic solution. Under more severe conditions (in the presence of aniline or on a silica gel t.l.c. plate) chloride ion displacement did take place with the formation of (3; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>) and mixtures of (5 and 6; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>) respectively.

In basic solution (pH > 7) the changeover in mechanism from rate-determining azocarbonium ion formation to base catalysed 1,3-dipolar ion (15)–(18) formation resulted in a second change in product. In this pH region in addition to the triazolotriazole (5), increasing amounts of the isomeric material (6) were formed as the basicity of the medium was increased. No hydrazide (4) was detected (by t.l.c.) in this region. The 1,3-dipolar ion (15) formed by rapid loss of bromide ion from the anion (14), can also be written as a 1,5-dipolar ion (16) [or by tautomerisation of the NH proton as (17) or (18)]. [1,5] Dipolar cycloaddition then gives the cyclic materials (5) and (6). Because of the stabilisation involved in triazole anion formation in (18), this may be the major form of the intermediate species formed. Control experiments under the reaction conditions used for the cyclisation of (2) in basic solution showed that the products (5) and (6) are not interconvertible. Also the hydrazide (4) is not cyclised to (5) or (6) (*vice versa*) under these conditions. It is interesting that LTA oxidation of (1) gives (6) exclusively, since it has been suggested that oxidation of aldehydic hydrazones proceeds *via* intermediate 1,3-dipolar ion formation.<sup>17</sup>

Thus it appears that intramolecular reaction of the 1,2,4-triazole ring with a carbonium ion centre is very sensitive to the species undergoing reaction. When the triazole ring is protonated no intramolecular reaction occurs; the neutral triazole reacts at N-4 yielding (5) exclusively while the triazole anion gives largely reaction at N-1, forming (6). It has been estimated that N-4 is the most basic centre in the 1,2,4-triazole system.<sup>18</sup> Presumably this factor is sufficient to overcome the considerable steric repulsion between the two aromatic rings in (5). An analogous intermolecular reaction which has received extensive study is the alkylation of basic heterocyclics (*e.g.* aminotetrazoles);<sup>19</sup> it has been shown that the neutral material and its conjugate base may have different alkylation sites.<sup>20</sup>

Although (5) may be isolated in good yield in neutral solution we have not been able using various reaction conditions to obtain (6) as the sole reaction product. The relative amounts of (5) and (6) formed are dependent on the ratio of substrate [(2,HBr)]:[HO<sup>-</sup>] (Table 4). This probably is a result of the very high reactivity of (2) in this region; even with the rapid stirring employed the addition of (2) as a hydrobromide salt would

cause a local reduction in the pH [consequently increasing formation of (5)]. However the isolation of the isomer (6) at high pH was facilitated by its lower solubility. When the reaction solution was acidified the material which precipitated was largely (6) (see Experimental section). Separation of the reaction mixture, using preparative t.l.c. showed, however, that (6) was the major product formed at the highest base concentrations employed (Table 4).

TABLE 4

Variation in ratio of isomeric triazolotriazoles formed from (2,HBr; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>) in the presence of base

Substrate [(2,HBr)]: [Base]	(5) (%) <sup>a</sup>	(6) (%)
1:4 <sup>b</sup>	90	10
1:4 <sup>c</sup>	63	37
1:20 <sup>c</sup>	33	67

<sup>a</sup> Total recovered yield of (5) + (6) is *ca.* 85% in each case, using preparative t.l.c.; the amounts were estimated from one experiment in each case. <sup>b</sup> Base = sodium carbonate.

<sup>c</sup> Base = sodium hydroxide.

#### EXPERIMENTAL

M.p.s were measured on an Electrothermal apparatus. I.r. spectra were measured on Perkin-Elmer 137E or 257 spectrophotometers. U.v. spectra were measured (unless otherwise stated) using a Unicam SP 800B spectrophotometer with 95% ethanol as solvent.

**Materials.**—Deionised water was twice distilled from alkaline potassium permanganate. Dioxan was AnalaR grade and was used without further purification. All inorganic materials were AnalaR grade; potassium bromide and sodium bromide were dried at 120° before use.

**Substrates.**—*Benzylidene-N-(5-phenyl-1,2,4-triazol-3-yl)-hydrazine*. S-Methylisothiuronium sulphate (6.95 g) was slowly added to a well agitated, ice-cold solution of 1.0N-sodium hydroxide (50 ml). Benzohydrazide (6.75 g) was added and the solution was left at room temperature for 5 days. The mixture (some precipitation had occurred) was heated at 50° for 3 h, cooled, and neutralised by addition of carbon dioxide. Benzamidoguanidine (6.4 g, 72%), m.p. 180–181°, was precipitated. The guanidine on recrystallisation from absolute ethanol had m.p. 184° (decomp.) (lit.,<sup>10</sup> 184°). Benzamidoguanidine (6 g) was refluxed in water (300 ml) for 3 h. On cooling 3-amino-5-phenyl-1,2,4-triazole (4.75 g, 88%) precipitated, m.p. 191–192° (lit.,<sup>21</sup> 190–191°). To 3-amino-5-phenyl-1,2,4-triazole (8.0 g) suspended in water (80 ml) was added concentrated hydrochloric acid (10 ml) and the resulting solution was cooled to 0°. A solution of sodium nitrite (7.0 g) in water (15 ml) was added and the mixture was maintained at 0° by the addition of ice. The precipitated yellow diazonium chloride was filtered off through a cooled filter funnel and washed with ice-water. To a suspension of the diazonium chloride in ice-water was added a solution of stannous chloride (26.7 g) in concentrated hydrochloric acid (16 ml). The mixture was stirred for a further 1 h and then heated at 35° to obtain a clear solution. On basification (20% sodium carbonate solution), the precipitated tin hydroxide was filtered off and the clear

<sup>16</sup> F. L. Scott, D. A. Cronin, and J. K. O'Halloran, *J. Chem. Soc. (C)*, 1971, 2769.

<sup>17</sup> W. A. F. Gladstone, J. B. Aylward, and R. O. C. Norman, *J. Chem. Soc. (C)*, 1969, 2587.

<sup>18</sup> K. T. Potts, *Chem. Rev.*, 1961, 61, 87.

<sup>19</sup> R. N. Butler and F. L. Scott, *J. Chem. Soc. (C)*, 1967, 239; *J. Org. Chem.*, 1967, 32, 1224.

<sup>20</sup> F. L. Scott and J. C. Tobin, *J. Chem. Soc. (C)*, 1971, 703.

<sup>21</sup> E. A. Markey, M.Sc. Thesis, National University of Ireland.

filtrate acidified with acetic acid. To the filtrate was added benzaldehyde (5 ml) in absolute ethanol (20 ml), to precipitate benzylidene-*N*-(5-phenyl-1,2,4-triazol-3-yl)-hydrazine (11.7 g, 88%), m.p. 230–235°. On recrystallisation from 95% ethanol the hydrazone had m.p. 237° (lit.,<sup>22</sup> 233°). The other substituted benzylidene hydrazines (1; Ar = XC<sub>6</sub>H<sub>4</sub>) were prepared similarly from the triazolyl-hydrazine and appropriate substituted benzaldehyde and had the following m.p. and analytical data: X = *p*-MeO (77% yield), m.p. 205° (lit.,<sup>10</sup> 195°); *p*-Me (87%), 236° (Found: C, 68.8; H, 5.5; N, 25.2. C<sub>16</sub>H<sub>15</sub>N<sub>5</sub> requires C, 69.3; H, 5.4; N, 25.3%); *p*-Me<sub>2</sub>CH (85%), 217–218° (Found: C, 70.35; H, 6.05; N, 23.2. C<sub>18</sub>H<sub>19</sub>N<sub>5</sub> requires C, 70.8; H, 6.2; N, 22.95%); *p*-Cl (85%), 258° (from water-ethanol-acetic acid) (Found: C, 60.0; H, 4.2; N, 23.3. C<sub>15</sub>H<sub>12</sub>ClN<sub>5</sub> requires C, 60.5; H, 4.0; N, 23.5%); *p*-Br (81%), 257° (Found: C, 52.2; H, 3.5; N, 20.5. C<sub>15</sub>H<sub>12</sub>BrN<sub>5</sub> requires C, 52.65; H, 3.5; N, 20.5%); *p*-NO<sub>2</sub> (85%), 273° (from acetic acid) (Found: C, 58.3; H, 3.8; N, 27.2. C<sub>15</sub>H<sub>12</sub>N<sub>6</sub>O<sub>2</sub> requires C, 58.4; H, 3.9; N, 27.3%); *m*-NO<sub>2</sub> (99%), 260–261° (from aqueous acetic acid) (Found: C, 58.3; H, 3.85; N, 27.7. C<sub>15</sub>H<sub>12</sub>N<sub>6</sub>O<sub>2</sub> requires C, 58.4; H, 3.9; N, 27.3%); *m*-Cl (85%), 245° (from water-ethanol-acetic acid) (Found: C, 60.0; H, 4.1; N, 24.0. C<sub>15</sub>H<sub>12</sub>ClN<sub>5</sub> requires C, 60.5; H, 4.1; N, 23.5%); *m*-Br (80%), 253° (from water-ethanol-acetic acid) (Found: C, 53.15; H, 3.9; N, 20.9. C<sub>15</sub>H<sub>12</sub>BrN<sub>5</sub> requires C, 52.65; H, 3.5; N, 20.5%).

**Bromination of hydrazones (1).** The following is a typical example. To a solution of (1; Ar = Ph) (1.0 g) in glacial acetic acid (60 ml) was added a solution of bromine (0.4 ml) in glacial acetic acid (10 ml) over 30 min. The mixture was stirred for a further 4 h by which time the hydrobromide of *N*-(5-phenyl-1,2,4-triazol-3-yl)benzohydrazonyl bromide (2; Ar = Ph) (1.55 g, 94%) precipitated. It was extracted (Soxhlet extractor) with boiling carbon tetrachloride and had m.p. 207° (lit.,<sup>23</sup> 203–205°). The other hydrazonyl bromide hydrobromides (2, HBr; Ar = XC<sub>6</sub>H<sub>4</sub>) were similarly prepared; when X was *p*-MeO, *p*-NO<sub>2</sub>, and *m*-NO<sub>2</sub> best yields were obtained by brominating a suspension of the hydrazone in acetic acid: X = *p*-MeO (80% yield), m.p. 207° (Found: C, 42.3; H, 3.4; Br, 34.9; N, 15.6. C<sub>16</sub>H<sub>15</sub>Br<sub>2</sub>N<sub>5</sub>O requires C, 42.4; H, 3.3; Br, 35.3; N, 15.45%); *p*-Me (95%), 216–218° (Found: C, 44.0; H, 3.5; Br, 36.15; N, 16.0. C<sub>16</sub>H<sub>15</sub>Br<sub>2</sub>N<sub>5</sub> requires C, 43.9; H, 3.4; Br, 36.6; N, 16.0%); *p*-Me<sub>2</sub>CH (81%), 208–210° (Found: C, 46.1; H, 4.05; Br, 34.4; N, 15.1. C<sub>18</sub>H<sub>19</sub>Br<sub>2</sub>N<sub>5</sub> requires C, 46.45; H, 4.1; Br, 34.4; N, 15.05%); *p*-Cl (94%), 230° (Found: C, 39.5; H, 2.7; Br, 34.8; N, 15.5. C<sub>15</sub>H<sub>12</sub>Br<sub>2</sub>ClN<sub>5</sub> requires C, 39.3; H, 2.6; Br, 35.0; N, 15.3%); *p*-Br (95%), 231–232° (Found: C, 36.1; H, 2.5; Br, 48.0; N, 14.0. C<sub>15</sub>H<sub>12</sub>Br<sub>3</sub>N<sub>5</sub> requires C, 35.85; H, 2.4; Br, 47.8; N, 13.9%); *p*-NO<sub>2</sub> (85%), 259–261° (Found: C, 38.0; H, 2.7; Br, 34.45; N, 18.3. C<sub>15</sub>H<sub>12</sub>Br<sub>2</sub>N<sub>6</sub>O<sub>2</sub> requires C, 38.5; H, 2.6; Br, 34.2; N, 17.95%); *m*-NO<sub>2</sub> (94%), 251–252° (Found: C, 37.95; H, 2.9; Br, 34.15; N, 18.3. C<sub>15</sub>H<sub>12</sub>Br<sub>2</sub>N<sub>6</sub>O<sub>2</sub> requires C, 38.5; H, 2.6; Br, 34.2; N, 17.95%); *m*-Br (85%), 234° (Found: C, 36.0; H, 2.7; Br, 48.3; N, 14.2. C<sub>15</sub>H<sub>12</sub>Br<sub>3</sub>N<sub>5</sub> requires C, 35.85; H, 2.4; Br, 47.8; N, 13.9%).

The hydrazonyl bromide free bases were isolated as follows. The benzohydrazonyl bromide hydrobromide (2, HBr; Ar = Ph) (0.50 g) was added to water (50 ml) and ether (50 ml) and agitated for 2 min. The material (93 mg), m.p. 163–168°, which remained suspended in the

etheral layer was filtered off. Titration of the aqueous layer showed 53% bromide ion liberation (based on two equivalents of bromine released per mole). The dried etheral layer was evaporated to give a yellow material (307 mg), m.p. 164–168°. Soxhlet extraction (with carbon tetrachloride) of this and the material which precipitated from ether gave *N*-(3-phenyl-1,2,4-triazol-3-yl)benzohydrazonyl bromide (2; Ar = Ph), m.p. 170° (decomp.) (Found: C, 52.8; H, 3.3; Br, 23.05; N, 20.4. C<sub>15</sub>H<sub>12</sub>BrN<sub>5</sub> requires C, 52.6; H, 3.5; Br, 23.4; N, 20.5%). The i.r. spectrum (KBr disc) of the hydrazonyl bromide free bases showed an absorption assigned to C=N at 1600–1630 cm<sup>-1</sup>; this absorption is at 1660–1680 cm<sup>-1</sup> in the hydrobromide salt.

The other hydrazonyl bromides (2; Ar = XC<sub>6</sub>H<sub>4</sub>) were similarly prepared: X = *p*-Me, m.p. >230° (Found: C, 53.4; H, 3.9; N, 19.2. C<sub>16</sub>H<sub>14</sub>BrN<sub>5</sub> requires C, 53.9; H, 4.0; N, 19.7%); *p*-Br, 207–208° (Found: C, 43.0; H, 2.7; Br, 37.5; N, 16.8. C<sub>15</sub>H<sub>11</sub>Br<sub>2</sub>N<sub>5</sub> requires C, 42.75; H, 2.6; Br, 38.0; N, 16.6%); *p*-NO<sub>2</sub>, 265–270° (Found: C, 46.7; H, 3.3; N, 21.7. C<sub>15</sub>H<sub>11</sub>BrN<sub>6</sub>O<sub>2</sub> requires C, 46.5; H, 2.9; N, 21.7%); *m*-Br, 211–212° (Found: C, 41.9; H, 3.2; N, 15.7. C<sub>15</sub>H<sub>11</sub>Br<sub>2</sub>N<sub>5</sub> requires C, 42.75; H, 2.6; N, 16.6%).

#### Reactions of Hydrazonyl Bromides (2) with Nucleophiles.—

(a) *With aniline.* The *p*-bromobenzohydrazonyl bromide (2; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>) (0.50 g) was stirred into a paste with aniline (1.5 ml), and heated at 60° for 5 min. On cooling a deep red solution was obtained; ether (30 ml) and water (2 × 10 ml) were added to remove aniline hydrobromide. The dried etheral extracts were evaporated and the residue dissolved in hot ethanol (10 ml) and on cooling water (10 ml) was added cautiously to precipitate the crude anilide (3; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>), m.p. 199–217°. Several recrystallisations from benzene raised the m.p. of the anilide to 220° (decomp.) (Found: C, 58.1; H, 4.1; Br, 18.4; N, 19.1. C<sub>21</sub>H<sub>17</sub>BrN<sub>6</sub> requires C, 58.2; H, 3.9; Br, 18.5; N, 19.4%).

(b) *With morpholine.* The *p*-nitrobenzohydrazonyl bromide (2; Ar = *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) (0.40 g) was made into a paste with AnalaR morpholine (1.0 ml). The mixture was heated at 60° for 5 min and then poured onto ice-cold water (20 ml). The red precipitate was collected and dried to give a dark brown gum. This was treated with cold acetone (5 ml) and the mixture left at 0° for 2 h. The precipitated material (0.20 g), m.p. 198–200°, was recrystallised from aqueous ethanol to give the morpholide (59%), m.p. 206–208° (Found: C, 57.9; H, 5.0; N, 24.6; O, 12.6. C<sub>19</sub>H<sub>19</sub>N<sub>7</sub>O<sub>3</sub> requires C, 58.0; H, 4.8; N, 24.9; O, 12.2%).

(c) *With water.* The *p*-bromobenzohydrazonyl bromide hydrobromide (2, HBr; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>) (1.0 g) was dissolved in 4 : 1 acetone–water (250 ml) at 0°, and left for 15 h. (Preliminary experiments indicated two equivalents of Br<sup>-</sup> were released under these conditions.) The solution was concentrated under reduced pressure at 50° to 55 ml. On standing at 0° for 24 h, a pale yellow solid (0.69 g) precipitated, m.p. 201–228°. The solid was extracted with benzene (200 ml) for 10 h using a Soxhlet apparatus. The benzene-insoluble fraction (470 mg), m.p. 261–263°, was recrystallised from aqueous ethanol to give *N*-*p*-bromobenzoyl-*N'*-(5-phenyl-1,2,4-triazol-3-yl)hydrazine (4; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>) in 70% yield, m.p. 263° (Found: C, 49.8; H, 3.3; Br, 22.6; N, 19.6; O, 4.7. C<sub>15</sub>H<sub>12</sub>BrN<sub>5</sub>O requires C,

<sup>22</sup> M. Manchot, *Ber.*, 1910, **43**, 1313.

<sup>23</sup> F. L. Scott and J. B. Aylward, *Tetrahedron Letters*, 1965, 841.

50.3; H, 3.35; Br, 22.35; N, 19.55; O, 4.5%). The i.r. spectrum showed characteristic absorptions at 1675 (C=O) and 3300  $\text{cm}^{-1}$  (NH) and was almost identical with an unambiguously prepared sample of the *p*-chlorobenzoyl derivative (4; Ar = *p*-ClC<sub>6</sub>H<sub>4</sub>). The benzene filtrate from the Soxhlet extraction was concentrated to 5 ml and light petroleum (b.p. 40–60°) (50 ml) was added. The insoluble material on recrystallisation from aqueous ethanol gave 3-(*p*-bromophenyl)-5-phenyl-1*H*-s-triazolo[3,4-*c*]-s-triazole (5; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>) (18%), m.p. 255–256° (Found: C, 52.7; H, 3.0; Br, 23.2; N, 20.3. C<sub>15</sub>H<sub>10</sub>BrN<sub>5</sub> requires C, 52.9; H, 2.9; Br, 23.5; N, 20.6%). A mixed m.p. between this material and the hydrazide (above) gave a 20° depression. Its i.r. spectrum showed a strong band at 1625  $\text{cm}^{-1}$  (C=N) and was similar to, but not identical, with the isomeric 3-(*p*-bromophenyl)-6-phenyl-5*H*-s-triazolo[4,3-*b*]-s-triazole (6; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>).

The *p*-chlorobenzohydrazonyl bromide hydrobromide (2, HBr; Ar = *p*-ClC<sub>6</sub>H<sub>4</sub>) was hydrolysed in acetone–water under the same conditions to give *N*-(*p*-chlorobenzoyl)-*N'*-(5-phenyl-1,2,4-triazol-3-yl)hydrazine (4; Ar = *p*-ClC<sub>6</sub>H<sub>4</sub>) in 57% yield, m.p. 255–256° (as a monohydrate) (Found: C, 57.35; H, 3.7; Cl, 11.5; N, 22.6; O, 5.4; H<sub>2</sub>O, 5.2. C<sub>15</sub>H<sub>14</sub>ClN<sub>5</sub>O<sub>2</sub> requires C, 57.4; H, 3.8; Cl, 11.3; N, 22.3; O, 5.1; H<sub>2</sub>O, 5.4%). This hydrazide was also prepared unambiguously (also as a hydrate) from *p*-chlorobenzoyl chloride and 3-hydrazino-5-phenyl-1,2,4-triazole in dry pyridine.

The *p*-toluohydrazonyl bromide hydrobromide (2, HBr; Ar = *p*-MeC<sub>6</sub>H<sub>4</sub>) (1.5 g) was stirred at 0° in 4 : 1 acetone–water (100 ml) for 2 h. Water (100 ml) was added and the solution extracted with ether (4 × 100 ml). The dried ethereal extracts were evaporated to leave a gummy material (0.85 g) which was dissolved in acetone (5 ml) and left at 0° for 1 h. The solid which precipitated (0.10 g, 11%) proved to be 3-(*p*-tolyl)-6-phenyl-5*H*-s-triazolo[4,3-*b*]-s-triazole (5; Ar = *p*-MeC<sub>6</sub>H<sub>4</sub>), and m.p. and mixed m.p. 287–288° (lit.,<sup>8</sup> 287–288°).

The aqueous layer from the ethereal extraction was evaporated *in vacuo* and the residue treated with benzene (2 ml). The undissolved material was the isomeric 3-(*p*-tolyl)-5-phenyl-1*H*-s-triazolo[3,4-*c*]-s-triazole (1.5%), m.p. 244–245° (Found: C, 70.1; H, 4.9; N, 25.2. C<sub>16</sub>H<sub>13</sub>N<sub>5</sub> requires C, 69.8; H, 4.7; N, 25.4%).

(d) *Sodium carbonate in water.* The *p*-bromobenzohydrazonyl hydrobromide (2, HBr, Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>) (1.0 g) was dissolved in 4 : 1 acetone–water (250 ml) containing two equivalents (0.85 g) of sodium carbonate at 0°. The sodium carbonate was filtered after 30 min and the solution concentrated to 60 ml under reduced pressure (at 40°). The resulting suspension was acidified with concentrated hydrochloric acid and left for 15 h at 0°. The light brown solid which precipitated (0.56 g), m.p. 224–240°, to leave filtrate A was extracted with hot benzene (25 ml) to leave residue B. On cooling, the triazolo[4,3-*b*]triazole (6; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>) precipitated (2%), m.p. 325–327° from the benzene. Evaporation of the benzene and work-up of the residue with light petroleum (40–60°) gave the isomeric [3,4-*c*]-compound (5; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>) (19% yield). Residue B was similarly treated to give a further 35% of the triazolo[4,3-*b*]triazole (6; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>). The original acidic filtrate A was evaporated at 70° to 30 ml. On standing a light brown solid precipitated and was washed free of gum with acetone (145 mg), m.p. 245–250°. This was shown to be a further crop (21.5%, making 75% overall) of the

[3,4-*c*]-isomer (5; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>) and had m.p. 254–256° on recrystallisation from ethanol–water.

(e) *Sodium hydroxide in water.* The *p*-bromobenzohydrazonyl bromide hydrobromide (2, HBr; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>) (1.0 g) was dissolved in 4 : 1 acetone–water (250 ml) containing sodium hydroxide (two equivalents, 0.32 g) at 0° and left for 30 min. The solution was concentrated to 60 ml (at 40°) and on being allowed to stand at room temperature, a solid precipitated (to leave filtrate A), which was shown to be 3-(*p*-bromophenyl)-6-phenyl-5*H*-s-triazolo[4,3-*b*]-s-triazole (34%), m.p. 325–327° on recrystallisation from aqueous acetic acid. Filtrate A was acidified (hydrochloric acid) and on work-up yielded a further quantity of the [4,3-*b*]-compound (2%) and the isomeric material (5; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>), m.p. 256–257° (11.5%).

(f) *Sodium acetate in water.* The benzohydrazonyl bromide hydrobromide (2, HBr; Ar = Ph) (1.4 g) was stirred in 4 : 1 acetone–water (60 ml) containing sodium acetate (1.6 g, two equivalents) at 0° for 20 min. Some gum which separated was filtered off, ice–water (40 ml) was added and the solution left at 0° for 15 h. The yellow precipitate (filtrate A) proved to be 3,5-diphenyl-1*H*-s-triazolo[3,4-*c*]-s-triazole (5; Ar = Ph) (64%), m.p. 264° (decomp.) (from aqueous ethanol) (lit.,<sup>7</sup> 272°) (Found: C, 68.7; H, 4.4; N, 26.8. Calc. for C<sub>15</sub>H<sub>11</sub>N<sub>5</sub>: C, 69.0; H, 4.2; N, 26.8%). A further 3% of the same material was obtained on work-up of the aqueous filtrate A.

*N*-(5-Phenyl-1,2,4-triazol-5-yl)-*p*-bromobenzohydrazonyl Chloride.—To 85% dioxan (40 ml) containing 0.1*M*-HCl was added 104 mg ( $2 \times 10^{-4}$  mol) of compound (2, HBr; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>). The mixture was stirred at room temperature for 15 h. To the resultant light yellow solution was added 40 ml of ether–H<sub>2</sub>O (1 : 1). After separation the aqueous layer was further extracted with ether (20 ml). The combined ether layers were then extracted with H<sub>2</sub>O (3 × 10 ml), dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated to an oily residue under reduced pressure. This was dissolved in a few drops of CHCl<sub>3</sub> and solidified by the addition of pentane (10 ml) to give the *hydrazonyl chloride* (64 mg, 85%) decomposes at 108–115° (Found: C, 46.7; H, 3.05; Br, 21.15; Cl, 9.15; N, 18.25. C<sub>15</sub>H<sub>11</sub>BrClN<sub>5</sub> requires C, 47.8; H, 2.9; Br, 21.25; Cl, 9.4; N, 18.6%). The u.v. (in acid solution) and i.r. spectra of the chloride were similar to those of the corresponding hydrazonyl bromide. The chloride was cyclised to a mixture of the triazolo[4,3-*b*]triazoles (5) and (6) on silica gel (t.l.c.) using chloroform–methanol (100 : 8.5). Reaction with aniline gave the anilide (3; Ar = *p*-BrC<sub>6</sub>H<sub>4</sub>) obtained from the corresponding hydrazonyl bromide.

*Kinetic Studies.*—The solvolyses of the benzohydrazonyl bromides (2) were studied in 85 : 15 (v/v) dioxan–water, usually at 25°. In all cases the ionic strength was maintained at 0.05*M* by the addition of sodium perchlorate. The rates of disappearance of the starting bromides were followed by measuring the change in the u.v. spectrum at suitable wavelengths. For buffered solutions, a Unicam SP 800 spectrophotometer was used, equipped with a thermostatted cell compartment, scale expander, and external recorder. For unbuffered solutions a pH-stat assembly mounted in the cell compartment of a Cary 14 u.v. spectrophotometer was used.<sup>15</sup> In each case the 'pH' values quoted were obtained by standardising the electrode (Metrohm EA 125U) in aqueous buffers at 25° using a Radiometer pH meter (PHM 28) and then reading off the values obtained in dioxan–water. In general the values

were reproducible if the electrode was allowed to steep in the dioxan-water for 30 min before measurements were taken. In those cases in which buffers (usually acetic acid-acetate) were used, separate experiments at constant pH but varying buffer concentration indicated the absence of buffer catalysis. In any event, the buffer concentrations were maintained at 0.01M. The pH values were

also checked at the end of a kinetic run, and any runs showing pH drift were neglected. The individual rate constants (which were shown in repeat experiments to have a precision of  $\pm 5\%$ ) were calculated either using the experimental infinity value of the absorbance or by the method of Guggenheim.

[3/2056 Received, 8th October, 1973]