A Free-radical Analogue of the Chapman Rearrangement; Conversion of Arylhydrazonates into *N'N'*-Diarylhydrazides

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Aryl *N*-(aryl)benzohydrazonates with substituents in the *C*-, *N*-, and *O*-aryl rings have been prepared from the corresponding hydrazonyl halides and substituted sodium phenoxide in benzene. The hydrazonates were shown to undergo rearrangement to *N'N'*-diarylbenzohydrazides on heating either alone or in the presence of a solvent. Radical initiators and oxidizing agents (*e.g.* manganese dioxide) catalyse the rearrangement. The intramolecularity of the rearrangement was demonstrated by the absence of cross-over products and the observation that the configuration of the migrating group is retained. Kinetic experiments have shown that electron-withdrawing substituents in each of the aromatic rings reduce the rate of rearrangement, the effect being greatest in the *N*-aryl ring where $\rho = -2{\cdot}1$. A mechanism involving radical initiated hydrogen abstraction followed by a 1,4-group migration to give a more stable hydrazyl free radical is proposed. *O*-Alkyl hydrazonates failed to isomerise under these conditions as did the *S*-aryl thio-analogues and the *N*-aryl nitrogen analogues. The *N'N'*-diarylhydrazides were hydrolysed in concentrated acid to the corresponding *NN*-diarylhydrazines, providing a route to these materials which are otherwise difficult to obtain, particularly when the aryl groups are dissimilar.

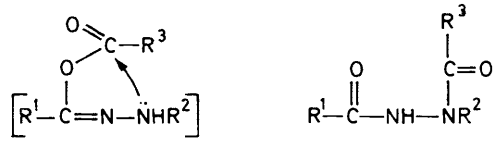
THE conversion of aryl imidates (1) into substituted amides (2) on heating is known as the Chapman rearrangement.[1-3] Interest in the rearrangement has centred on its synthetic utility [4] and on the mechanism of the interconversion. The intramolecularity of the rearrangement was first suggested by Chapman [3] and subsequent work has confirmed this. Thus Wiberg and Rowland [5] found that when a mixture of two aryl imidates (1; $R^1 = R^2 = R^3 = Ph$) and (1; $R^1 = Ph$; $R^2 = R^3 = p\text{-}ClC_6H_4$) was heated, just two amides resulted, no cross-over products being detected. More recent work by Wheeler [6] using radioactive labelling of the migrating

(1) (2)

group was also consistent with the intramolecular mechanism.

The rearrangement of alkyl imidates occurs under more forcing conditions and usually in the presence of acidic catalysis.[7-9] The mechanism of rearrangement in this case appears to be different, and kinetic studies suggest an intermolecular alkylation mechanism for the acid catalysed process.[10] Acyl imidates (1; R^3 = Ac or Bz) rearrange to the corresponding imides (2; R^3 = Ac or Bz) very readily and can be isolated only when the imidate is stabilized by special structural features.[11,12] The corresponding rearrangement of *O*-acylhydrazonates (3) to *N'*-acylhydrazides (4) is also apparently facile and the latter is the only product which has been isolated.[13,14]

We have now synthesised the corresponding arylhydrazonates (5) [analogues of (1)] and have found that they are smoothly converted on heating alone or in the presence of a solvent into the corresponding *N'N'*-disubstituted hydrazides (6). This report examines the scope and mechanism of this novel rearrangement.[15]



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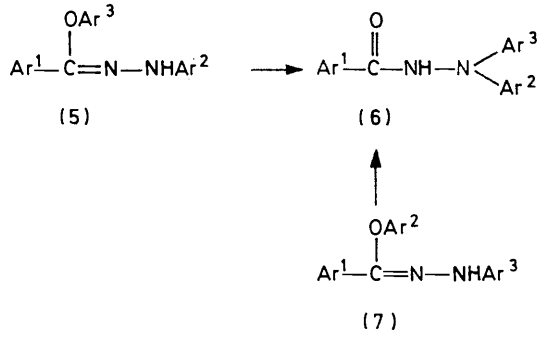


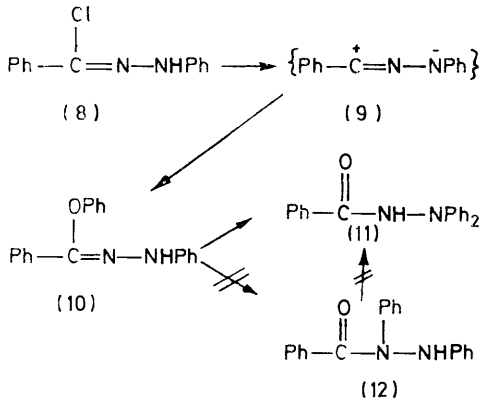
(5) (6) (7)

RESULTS AND DISCUSSION

Formation of Hydrazonate.—Treatment of *N*-phenylbenzohydrazonyl chloride (8) with phenol in benzene in the presence of triethylamine (or, better, with sodium phenoxide in the same solvent) results in the formation of phenyl *N*-phenylbenzohydrazonate (10). This was

[1] W. Wislicenus and M. Goldschmidt., *Ber.*, 1900, **33**, 1470.
[2] O. Mumm, H. Hesse, and H. Volquartz, *Ber.*, 1915, **48**, 379.
[3] A. W. Chapman, *J. Chem. Soc.*, 1925, **127**, 1992.
[4] J. W. Schulenberg and S. Archer, *Org. Reactions*, 1965, **14**, 1.
[5] K. B. Wiberg and B. I. Rowland, *J. Amer. Chem. Soc.*, 1955, **77**, 2205.
[6] O. H. Wheeler, *J. Org. Chem.*, 1969, **34**, 966.
[7] G. D. Lander, *J. Chem. Soc.*, 1903, **83**, 406.
[8] R. M. Roberts and P. J. Vogt, *J. Amer. Chem. Soc.*, 1956, **78**, 4778.
[9] F. Crammer and N. Hennrich, *Ber.*, 1961, **94**, 976.
[10] B. C. Challis and A. D. Frenkel, *J.C.S. Chem. Comm.*, 1972, 303.
[11] D. Y. Curtin and L. L. Millar, *J. Amer. Chem. Soc.*, 1967, **89**, 637.
[12] J. P. Schwarz, *J. Org. Chem.*, 1972, **37**, 2906.
[13] W. A. F. Gladstone, J. B. Aylward, and R. O. C. Norman, *J. Chem. Soc.* (*C*), 1969, 2587.
[14] J. T. Edward and S. A. Samad, *Canad. J. Chem.*, 1963, **41**, 1638.
[15] Portions of this work have appeared as communications; A. F. Hegarty, J. A. Kearney, M. Cashman, and F. L. Scott, *Chem. Comm.*, 1971, 689; A. F. Hegarty, J. A. Kearney, and F. L. Scott, *Tetrahedron Letters*, 1972, 3211.

found to be a very general reaction and good yields of hydrazonates were obtained when hydrazonyl halides with various substituents in the *N*- or *C*-aryl rings were used or when the phenol itself was substituted. The halides of type (8) were themselves available either by bromination of the parent aldehyde hydrazone (when the *N*-aryl ring was substituted so as to minimize polysubstitution [16]) or by treatment of *N'*-arylbenzohydrazides with phosphorus pentachloride. The mechanism of the formation of (10) most likely involves initial base catalysed dehydrohalogenation [17] of the chloride to give the 1,3-dipolar ion species (9), followed by addition of



phenol. The hydrazonates were generally stable when stored at ambient temperature, and could be recrystallised if the solvent temperature was maintained below 60°.

The hydrazonate structure (10) for the products, rather than the isomeric *N'N'*-diphenylhydrazide (11) or *NN'*-diphenylhydrazide (12) was indicated by the absence of absorptions in the i.r. spectrum in the region 1610—1800 cm^{-1}. The hydrazides (11) and (12) were also synthesised independently and shown to be different (i.r. and u.v. spectra, m.p.s) from (10).

Rearrangement of the Hydrazonates.—On heating the hydrazonate (10) at 200° for 10 min in the absence of solvent rearrangement occurred and the product [which had a C, H, N, and O analysis identical to that of (10)] was shown to be the *N'N'*-diphenylhydrazide (11) rather than the ' normal ' Chapman product (12). The products (11) are characterized by sharp m.p.s and by a strong i.r. absorption, typical of arylhydrazides,[18] at 1670 cm^{-1}. The possibility arises that the rearrangement of (10) to (11) is stepwise, involving the initial formation of (12), followed by slow isomerisation of (12) to (11). Under these conditions there would be a build-up of (12) during the isomerisation. This was shown not to be the case since the *NN'*-diphenylhydrazide (12) was stable at 200° for 30 min and did not undergo rearrangement. Moreover, when the rearrangement of (10) was allowed to proceed partially (1 min at 200°), t.l.c. of the products obtained showed that only (10) and (11) were present and no isomeric hydrazide (12) was detectable. These and other data presented below make the recent claim [19] that arylhydrazonates undergo rearrangement to *NN'*-diarylhydrazides of type (12), most unlikely.

The rearrangement was shown to be quite general, with a variety of hydrazonates (5) with substituents in the aryl rings Ar^1—Ar^3 undergoing conversion into the hydrazides (6) in good yield (see Experimental section). Those hydrazonates in which electron-withdrawing groups were present (especially $Ar^2 = p\text{-}NO_2C_6H_4$) required a longer reaction time (1 h) and consequently some decomposition took place.

Intramolecularity of Rearrangement.—The migrating group [Ar^3 in (5)] retained its configuration during migration *i.e.* the ring carbon originally attached to oxygen in (5) was attached to nitrogen in (6). Thus rotation of the migrating group [so that for example a *p*- became an *m*- or *o*-bromophenyl group in (6)] was precluded. This was shown by the identity of products obtained on rearranging (separately) pairs of isomeric hydrazonates (5) and (7) in which the aryl groups attached to oxygen and nitrogen were reversed. In each case studied (see Table 1 for m.p. data; the products were also identified by i.r. spectroscopy and t.l.c. analysis) the same hydrazide [*i.e.* (6)] was obtained by both routes. This also confirms that the rearranged hydrazides have the *N'N'*-diaryl structure (6) rather than their being *NN'*-diarylhydrazides; in the latter case, rearrangement of (5) and of (7) would yield different products.

TABLE 1

M.p. data showing the identity of the hydrazides obtained on rearrangement of isomeric hydrazonates (5) and (7) (in each case $Ar^1 = Ar^2 = Ph$)

Substituent Ar^3	M.p. (°C) Hydrazonate (5)	Hydrazonate (7)	Hydrazide (6)
Ph	154—155	154—155	190
$p\text{-}ClC_6H_4$	137	104—108	168—170
$p\text{-}BrC_6H_4$	154—156	98—100	205—206
$p\text{-}MeC_6H_4$	181—183	108—110	171—173
$p\text{-}NO_2C_6H_4$	175—178	134	178—180

The hydrazonate–hydrazide rearrangement was also (within the limits of detection) intramolecular. This result was not unexpected in view of the retention of configuration experiments summarised in Table 1. When pairs of hydrazonates [*e.g.* (10) and (5; $Ar^1 = Ph$, $Ar^2 = Ar^3 = p\text{-}BrC_6H_4$)] were heated together at 200° no cross-over products were obtained [*e.g.* (11) and (6; $Ar^1 = Ph$; $Ar^2 = Ar^3 = p\text{-}BrC_6H_4$) were formed; no (6; $Ar^1 = Ar^2 = Ph$, $Ar^2 = p\text{-}BrC_6H_4$) was detected]. The products were separated by t.l.c. and trial runs with authentic samples of the possible products established that these would have been detected if they were present (at $\geqslant 5\%$). The separation was easy if the groups involved carried dissimilar substituents, *e.g.*

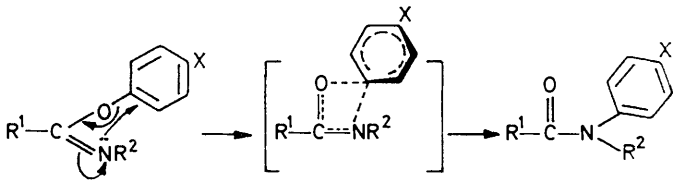
[16] A. F. Hegarty and F. L. Scott, *J. Chem. Soc.* (*B*), 1966, 672.
[17] A. F. Hegarty, M. Cashman, and F. L. Scott, *J.C.S. Perkin II*, 1972, 44.
[18] R. N. Butler and F. L. Scott, *J. Chem. Soc.* (*C*), 1966, 1202.
[19] A. S. Shawali and H. M. Hassaneen, *Tetrahedron Letters*, 1972, 1299.

p-BrC_6H_4, p-$NO_2C_6H_4$, or Ph, but more difficult if the groups involved were closely related, *e.g.* Ph and p-MeC_6H_4. Since in the latter case the migratory aptitudes are similar, cross-over if it occurs at all will be most likely detected in these cases. This difficulty was partly overcome by rearranging a mixture of (5) and (7) with, in each case, $Ar^1 = Ar^2 = Ph$ and $Ar^3 = p$-MeC_6H_4. If no cross-over occurred then a single product (6; $Ar^1 = Ar^2 = Ph$; $Ar^3 = p$-MeC_6H_4) would result; otherwise (6; $Ar^1 = Ph$; $Ar^2 = Ar^3 = p$-MeC_6H_4) and (11) would be also formed. In the event, neither of these could be detected in the reaction mixture, a single hydrazide being formed.

Formation of Diarylhydrazines.—The hydrazides (6) could be hydrolysed to the corresponding *NN*-diarylhydrazines in concentrated hydrochloric acid–ethanol. This provides an excellent method for the synthesis of unsymmetrical diarylhydrazines, particularly those in which the aryl groups are dissimilar. Alternative routes to these materials, usually from diarylamines, are tedious and low yields are obtained. In the case of the hydrolysis product from (11), it was shown to be an unsymmetrical rather than symmetrical diphenylhydrazine by ready formation of a benzylidene derivative. The hydrazine was also treated with benzoyl chloride to reform the starting hydrazide (11), showing that further phenyl group migration did not occur during hydrolysis.

Substituent Effects.—The phenylhydrazonate (10) also rearranged to (11) under mild conditions in the presence of a solvent. Thus, in refluxing xylene, toluene, and dioxan reaction was complete (as judged from the i.r. spectrum of the product and t.l.c. analysis of the reaction mixture) in 4 h. In benzene at reflux only partial rearrangement had occurred after 17 h. The order of reactivity in refluxing toluene can be judged from the times taken to complete *ca.* 95% rearrangement. For the hydrazonates (5; $Ar^1 = Ar^2 = Ph$) these were: 4 h ($Ar^3 = p$-$NO_2C_6H_4$); 3 h ($Ar^3 = Ph$); 0·5 h ($Ar^3 = p$-MeC_6H_4). It thus appears that, under these conditions, the presence of electron-withdrawing groups in the migrating ring Ar^3 *diminishes* the tendency of the hydrazonates (5) to rearrange to (6).

This result is surprising since it is in direct contrast to the well-documented substituent effects in the normal Chapman rearrangement of aryl imidates (1). In the case of (1), the rearrangement has been shown to follow first-order kinetics with the rate depending on the nature and position of substituents in the aromatic ring (R^3). Earlier results by Chapman [20] (who measured the rearrangement of molten salts in the absence of solvent) were confirmed by Wiberg and Rowland [5] who found that in diphenyl ether as solvent, the rearrangement was promoted by electron-withdrawing substituents in R^3 and retarded by these substituents in R^2. A mechanism involving nucleophilic displacement by the imide nitrogen atom on the migrating aromatic ring was suggested (Scheme 1). Further support for this mechanism has come from the good correlations obtained [5] when the log of observed constants for nucleophilic displacement by piperidine on p-substituted o-nitrochlorobenzenes is plotted against log k_{obs} for variation of X (Scheme 1) in the Chapman rearrangement of imidates.



SCHEME 1

To obtain quantitative data for the effect of substituents on the rearrangement of arylhydrazonates (5), the rearrangement was studied in 4 : 1 (v/v) dioxan–water at 97 °C. Each substrate (*ca.* 10^{-4}M) was made up at 25 °C in this solvent and then heated at 90 °C in sealed ampoules. The ampoules were cooled at appropriate intervals (the first point being taken after *ca.* 5 min at 97 °C) and analysed by recording the u.v. spectrum of the contents. In each case it was shown that the product obtained was the hydrazide (6) by (a) comparison of the u.v. spectrum of the reaction product with that of an authentic sample of the hydrazide under the same conditions, (b) t.l.c. analysis, and (c) isolation and recording the i.r. spectrum of the product. Moreover conversion of (5) into (6) occurred without the formation of intermediates which absorb in the u.v. region. This follows from the observation of tight isosbestic points in the u.v. spectrum (see Figure 1) for the conversion of (5) into (6). A further reaction of the product occurs on com-

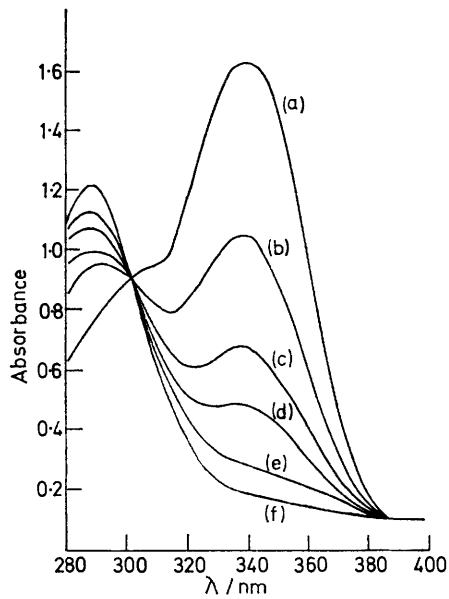


FIGURE 1 Repetitive scans of the u.v. region for the conversion of the hydrazonate (5; $Ar^1 = Ar^2 = Ph$, $Ar^3 = m$-ClC_6H_4) to the hydrazide (6; $Ar^1 = Ar^2 = Ph$, $Ar^3 = m$-ClC_6H_4) in 4 : 1 (v/v) dioxan–water at 97°: (a) $t = 0$; (b) 10; (c) 20; (d) 30; (e) 40 min; (f) $t = \infty$

[20] A. W. Chapman, *J. Chem. Soc.*, 1927, 1743.

pletion of rearrangement [this is most likely hydrolysis of the hydrazide (6)]. However, this was much slower than the rearrangements and the infinity values remained constant for 10—20 half-lives.

The results obtained are summarised in Table 2. Clearly electron-withdrawing substituents retard and

TABLE 2

Observed pseudo-first-order rate constants for the rearrangement of aryl *N*-arylbenzohydrazonates (5) to *N'N'*-diarylbenzohydrazides (6) in 4 : 1 (v/v) dioxan–water at 97°

Ar^1	Ar^2	Ar^3	$10^4k/s^{-1}$
Ph	Ph	Ph	25
p-MeC_6H_4	Ph	Ph	72
p-$NO_2C_6H_4$	Ph	Ph	4·0
p-ClC_6H_4	Ph	Ph	10
Ph	*p*-MeC_6H_4	Ph	64
Ph	*p*-ClC_6H_4	Ph	15
Ph	*p*-$NO_2C_6H_4$	Ph	0·65
Ph	Ph	*p*-MeC_6H_4	160
Ph	Ph	*p*-ClC_6H_4	20
Ph	Ph	*p*-$NO_2C_6H_4$	4·9
Ph	Ph	*m*-ClC_6H_4	11

electron-donating substituents enhance reactivity, independent of whether the substituent is in Ar^1, Ar^2, or Ar^3. A plot of log k_{obs} *vs.* the σ values of McDaniel and Brown [21] for substituent variation in the *N*-aryl ring (Ar^2) gave a ρ value of −2·07 ($r = 0.991$) for the rearrangement (Figure 2). Poorer correlations were obtained for substituent variation in the other aryl groups [*e.g.* $\rho = -1.24$ ($r = 0.970$) for substituent variation in Ar^1] but in general the ability of a given

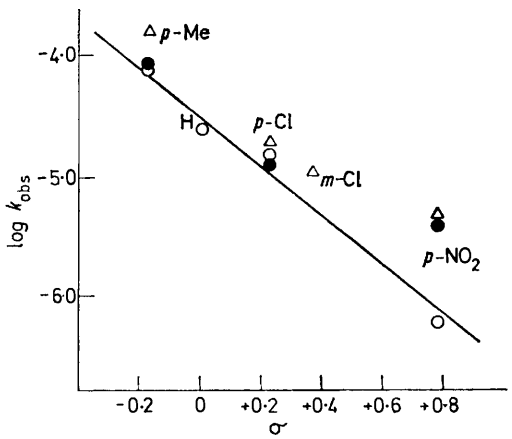


FIGURE 2 Plot of log k_{obs} for the rearrangement of phenyl *N*-arylbenzohydrazonates in 4 : 1 (v/v) dioxan–water at 97° *vs.* the σ value for the substituent. The datum points are given by open circles for the variation of the *N*-aryl substituent in the hydrazonates (5). Also included are data for effect of variation of the CAr^1 group (●) and OAr^3 group (△) on the rate of rearrangement of (5)

substituent to change the reactivity of the hydrazonate (5) was in the following order: $Ar^2 > Ar^1 \sim Ar^3$ (see Figure 2).

The kinetic results were reproducible (the values reported in Table 2 are averages from two or more runs with a standard deviation of ±5%) but only if the same batch of solvent was used and if the measurements were made within a limited time. The observed rate constants however varied (up to *ca.* 2-fold) from one batch of dioxan–water or when the solvent was 'aged' (stored for *ca.* 4 weeks). In an attempt to obviate this

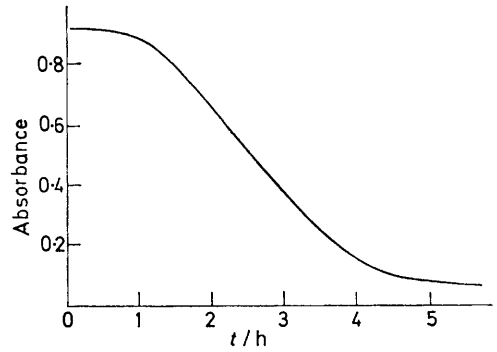


FIGURE 3 Plot of the observed optical density of (10) at 340 nm *vs.* time in 95% ethanol containing 10^{-4}M-hydrochloric acid at 75° (substrate concentration = 1.5×10^{-5}M)

problem the rearrangement was studied in 95% ethanol. At 75° in this solvent rearrangement of (10) to (11) occurred ($t_{\frac{1}{2}}$ *ca.* 2 h), but only in the presence of 10^{-4}M-hydrochloric acid (substrate concentration = 1.25×10^{-5}M). In the absence of added hydrochloric acid the hydrazonate appeared stable under these conditions; addition of 1×10^{-4}M-sodium hydroxide also inhibited rearrangement. Other acids (sulphuric or perchloric) did not catalyse rearrangement; neither did salts (sodium chloride, potassium chloride) which had a common anion.

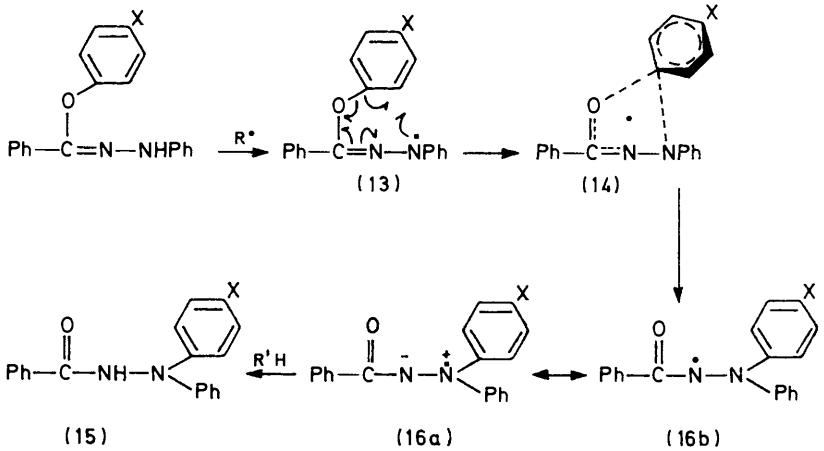
A typical optical density *vs.* time plot for the substrate (10) at 350 nm in 95% ethanol containing 10^{-4}M-hydrochloric acid is given in Figure 3. At this wavelength, only the starting hydrazonate (10) absorbs. It is seen that the concentration of (10) changes slowly at first, then rapidly before decaying exponentially. This behaviour is characteristic of an autocatalytic reaction,[22] and suggested, together with the evidence above, that the rearrangement was free radical initiated. This was confirmed as follows. In the presence of the radical inhibitor bis-(4-hydroxy-3-methyl-5-t-butylphenyl) sulphide (10^{-4}M), no rearrangement occurred. This was true when the inhibitor was added to 95% ethanol containing 10^{-4}M-hydrochloric acid and the substrate was then added or when the inhibitor was added when the rearrangement was already partially complete. The rearrangement was on the other hand catalysed (in the absence of added hydrochloric acid) by the free radical initiators benzoyl peroxide or azobisisobutyronitrile both at 10^{-4}M. As in the hydrochloric acid catalysed reactions (which could involve an impurity as initiator), plots of hydrazonate concentration *vs.* time showed apparent autocatalysis (see Figure 3), although much

[21] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.

[22] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' Wiley, New York, 1961, 2nd edn., p. 19.

reduced. Both initiated reactions gave the rearranged hydrazide (11) as the major product, but when higher concentrations of benzoyl peroxide were used several side-products were also obtained; these possibly result from coupling between phenyl radicals and the substrate or hydrazide product.

Mechanism of Rearrangement.—A radical initiated mechanism for the hydrazonate to hydrazide rearrangement is outlined in Scheme 2. The initiator (R·) removes the amino-hydrogen atom to give the hydrazonate

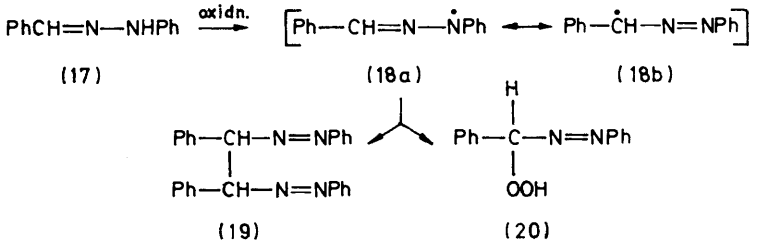


SCHEME 2

radical (13); this then undergoes intramolecular rearrangement [possibly *via* the bridged radical species (14)] to give the more stable hydrazyl radical (16). Hydrogen abstraction from the solvent or from another molecule of the substrate then gives the observed product, the hydrazide (15).

The initial formation of the radical (13) is not unreasonable in view of the considerable evidence in the literature that oxidation of ketone or aldehyde phenylhydrazones [*e.g.* (17)] occurs very readily. Oxidizing agents used include manganese dioxide,[23] pentyl nitrite,[24] iodine, mercuric oxide, ammoniacal silver nitrate in dimethylformamide,[25] or oxygen.[26] Complex products result but the initial materials formed are the dimer (19) and the hydroperoxide (20). A free radical mechanism has been proposed for the oxidations, with the intermediacy of (18); consistent with this is the observation that *NN*-disubstituted hydrazones do not undergo oxidative dimerisation.[26,27]

These oxidizing agents also catalyse the hydrazonate to hydrazide (5) ⟶ (6) rearrangement. The most satisfactory reagent was found to be activated manganese dioxide[28] in benzene; since the reaction is heterogeneous the reagent was easily separated by filtration. On stirring (10) at room temperature for 4 h in benzene with manganese dioxide, a complex mixture of products, including a small amount of hydrazonate (11), was obtained (as shown by t.l.c.). The other products, although not investigated are possibly dimeric or oxidation products formed from (13).[24] However, when MnO_2 was added to a solution of (10) in benzene and the mixture was refluxed, rearrangement to (11) was clean and essentially complete in 40 min. The other substituted materials (5) were also successfully rearranged by this convenient route. When the aryl rings (especially Ar^2) were substituted by electron-withdrawing substituents longer times were required to complete rearrangement (similar to the results obtained in dioxan, see Table 2).



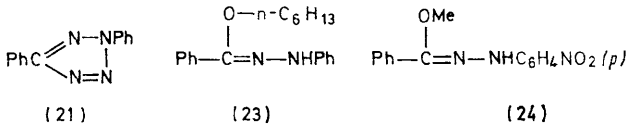
The manganese dioxide catalysed rearrangements showed the same intramolecular character as the therm-

[23] I. Behetnagae and M. V. George, *J. Org. Chem.*, 1967, **32**, 2252.
[24] H. Minato, H. Tateno, and H. Yokowawa, *Bull. Chem. Soc. Japan*, 1966, **39**, 2724.
[25] T. W. Milligan and B. C. Minor, *J. Org. Chem.*, 1962, **27**, 4663; C. Wintner and J. Wiecko, *Tetrahedron Letters*, 1969, 1595.
[26] E. G. E. Hawkins, *J. Chem. Soc.* (*C*), 1971, 1474; W. F. Taylor, H. A. Weiss, and T. J. Wallace, *J. Org. Chem.*, 1969, **34**, 1759; A. J. Bellamy and R. D. Guthrie, *J. Chem. Soc.*, 1965, 2788; Y. Yao and P. Resnick, *J. Org. Chem.*, 1965, **30**, 2832.
[27] R. F. Smith, J. A. Albright, and A. M. Waring, *J. Org. Chem.*, 1966, **31**, 4100.
[28] R. M. Evans, *Quart. Rev.*, 1959, **13**, 60.

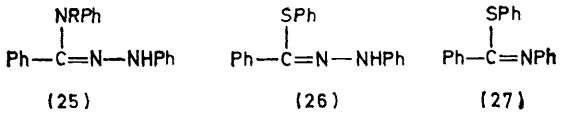
ally induced rearrangement. Thus as before no cross-over products were observed and identical products (6) were obtained on rearrangement of the two different hydrazonates (5) and (7). It seems possible therefore that the thermal rearrangement could also involve a free radical pathway.

The driving force for the rearrangement is probably the formation of the relatively stable hydrazyl radical (16). The stability of these free radicals has been investigated in detail by Goldschmidt and his co-workers.[29] Studies on the dissociation of the corresponding tetrazenes [30,31] have shown that electron-donating substituents (X) in the *N*-phenyl ring stabilize (16) while such substitution in the acyl moiety destabilizes (16). Appropriately substituted hydrazyl radicals (*e.g.* 2,2-diphenyl-1-picrylhydrazyl) are, in fact, indefinitely stable and do not dimerise to any appreciable extent. The substituent effects are explicable in terms of the contribution of structure (16a) to the stabilization of the free radical species; more recent e.s.r. measurements are consistent with this.[32,33] Wilmarth and Schwartz,[34] extending Goldschmidt's data, obtained a ρ value of $-1{\cdot}52$ ($r = 0{\cdot}994$) for the effect of the variation of substituent X on the equilibria for the dissociation of tetrazenes [formation of (16)]. The substituent effects on the rearrangement of hydrazonates are similar to this, both *N*-aryl and *O*-aryl [which on rearrangement to (16) also becomes an *N*-aryl group] having negative ρ values in the range $-1{\cdot}0$ to $-2{\cdot}1$. However electron-withdrawing substituents in the *C*-aryl ring, which would be expected [34] to stabilize the hydrazyl radical (16), decrease the rate of hydrazonate–hydrazide rearrangement. It is likely therefore that the initiation step [formation of the radical species (13)] is also important under the conditions which we have used to measure substituent effects. It is interesting that there is evidence that the ease of radical formation from hydrazones (17) is reduced when electron-withdrawing substituents are present in the *N*-aryl ring [*e.g.*, *N*-(*p*-nitrophenyl)- and *N*-(2,4-dinitrophenyl)-hydrazones are resistant to oxidation [26]].

Attempted Rearrangement of Hydrazonate Analogues.—Although aryl hydrazonates have not been previously reported, some *O*-alkyl analogues have been described. Interestingly, these do not appear to undergo facile rearrangement to isomeric hydrazides. Huisgen and his co-workers [35] found that reaction of 2,5-diphenyltetrazole (21) with hexan-1-ol at reflux gave the unrearranged hydrazonate (23) [formed by reaction of the alcohol with the 1,3-dipolar ion (9)]. Under the same conditions the product obtained on treating (21) with phenol at reflux was the hydrazide (11). Similarly, methyl *N*-(*p*-nitrophenyl)benzohydrazonate (24) has been reported [36] not to rearrange to *N'*-methyl-N'-*p*-nitrophenylbenzohydrazide; on heating at high temperatures extensive decomposition occurs. We have also attempted, without success, to rearrange the alkyl hydrazonate (24) using manganese dioxide as catalyst. This is entirely



(21) (23) (24)



(25) (26) (27)

consistent with the known reluctance of radical species to undergo 1,3-alkyl (as opposed to 1,3-aryl) group migrations.[37]

Attempts were also made to rearrange the nitrogen analogues (25) with R = H or Me. In the presence of radical initiators or on heating in dioxan at reflux (25) did not rearrange; on prolonged heating at 200°, extensive decomposition took place. The thiohydrazonate (26) was also investigated and under similar conditions no rearrangement to the isomeric *N'N'*-diphenyl(thiobenzohydrazide) was detected. The thioimidate (27) was investigated by Chapman,[38] and evidence that it undergoes rearrangement to *NN*-diphenyl(thiobenzamide) at 290° is indirect.

Acid Catalysed Hydrolysis of Hydrazonates.—In dioxan–water or ethanol–water the hydrazonate (10) also undergoes acid catalysed hydrolysis to form *N'*-phenylbenzohydrazide (32). The rate of hydrolysis is proportional to added acid concentration over the range 5×10^{-2}—1·0M (where $k_{obs} = 4{\cdot}4 \times 10^{-3}$ s^{-1} at 75°); hydrochloric, sulphuric, and perchloric acid all catalysed hydrolysis. The *N'N'*-diphenylhydrazide (11) does not undergo hydrolysis under these conditions; therefore the rearrangement does not precede hydrolysis. An acid catalysed hydrolytic mechanism is outlined in Scheme 3, where the acid acts to improve the leaving ability of phenoxide ion, giving the azocarbonium ion (29). The latter reacts with water to form the hydrazide (32).[39] The acid catalysed pathway appears to be the best method of converting (10) to (32). In basic solution, phenoxide ion is such a poor leaving group that elimination, even from the anion (30) to form the 1,3-dipolar ion (31), does not occur.[17]

[29] S. Goldschmidt, *Ber.*, 1920, **53**, 44; S. Goldschmidt and K. Euler, *ibid.*, 1922, **55**, 616; S. Goldschmidt and K. Renn, *ibid.*, p. 628; S. Goldschmidt and F. Graef, *ibid.*, 1928, **61**, 1858.
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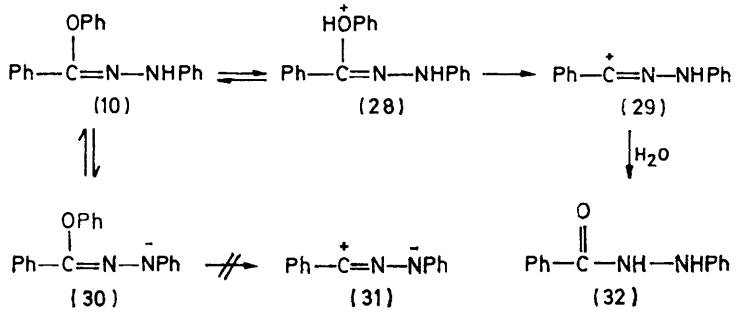
[39] F. L. Scott, M. Cashman, and A. F. Hegarty, *J. Chem. Soc.* (*B*), 1971, 1607.



SCHEME 3

EXPERIMENTAL

Phenyl N-phenylbenzohydrazonate.—Method A. Triethylamine (2·75 ml, 20 mmol) was slowly added with vigorous stirring over 1 h at room temperature to a solution of *N*-phenylbenzohydrazonyl chloride (2·30 g, 10 mmol) and phenol (0·94 g, 10 mmol) in dry benzene (150 ml). Stirring was continued for a further 2 h and the mixture was set aside overnight. The precipitated triethylamine hydrochloride (1·5 g, 75%) was filtered off and the filtrate concentrated under reduced pressure. The *hydrazonate* precipitated, m.p. 150—153° (0·94 g, 36%), and on recrystallization from n-hexane had m.p. 154—155° (Found: C, 79·1; H, 5·5; N, 8·7. $C_{19}H_{16}N_2O$ requires C, 79·1; H, 5·5; N, 9·1%).

Method B. Sodium hydride (0·48 g of a 50% dispersion in oil, 10 mmol) was slowly added with stirring to phenol (0·94 g, 10 mmol) in dry benzene (50 ml) to give a suspension of sodium phenoxide. The phenoxide was added over 1 h at room temperature to a solution of *N*-phenylbenzohydrazonyl chloride (2·30 g, 10 mmol) in dry benzene (150 ml) with vigorous stirring. The mixture was protected from moisture throughout. Stirring was continued for a further 0·5 h and the mixture was filtered to remove sodium chloride (0·49 g, 84%). The filtrate was evaporated under reduced pressure to precipitate the hydrazonate, m.p. 151—154° (2·40 g, 83%). Recrystallization was carried out as before from n-hexane. The other *aryl N-phenylbenzohydrazonates* were also prepared by this general method; analytical and m.p. data were as follows: *p*-Me, m.p. 162—164° (Found: C, 78·1; H, 5·8; N, 8·55. $C_{20}H_{18}N_2$ requires C, 79·5; H, 6·0; N, 9·3%); *p*-NO_2, 134° (Found: C, 68·4; H, 4·7; N, 12·4. $C_{19}H_{15}N_3O_3$ requires C, 68·5; H, 4·5; N, 12·6%); *p*-Cl, 108—110° (Found: C, 70·8; H, 4·9; N, 8·6. $C_{19}H_{15}ClN_2O$ requires C, 70·6; H, 4·6; N, 8·7%), *m*-Cl, 116° (Found: C, 71·55; H, 4·8; N, 8·8. $C_{19}H_{15}ClN_2O$ requires C, 70·8; H, 4·6; N, 8·7%).

Phenyl N-Phenyl-p-toluohydrazonate.—p-Toluoyl chloride (15·4 g, 0·1 mol) was added dropwise over 1 h at ambient temperature to a vigorously stirred solution of phenylhydrazine (10·8 g, 0·1 mol) in pyridine (200 ml). The mixture was added to crushed ice and after 4 h *N*-phenyl-*p*-toluohydrazide, m.p. 166—169° (20·6 g, 91%) precipitated. On recrystallization from ethanol this had m.p. 169°. The hydrazide (11·3 g, 50 mmol) and finely powdered phosphorus pentachloride (12·3 g, 60 mmol) were heated at reflux in dry ether (150 ml) for 16 h in an apparatus protected from moisture. To the clear solution obtained, phenol (20·0 g) in dry ether (50 ml) was added slowly with stirring. Methanol (20 ml) was then added slowly and the mixture was kept in a current of air for 4 h to remove the ether. The methanol was distilled off by slowly heating the reaction mixture until the internal temperature was 70°. The reaction mixture was then left overnight at 0° and *N*-phenyl-*p*-toluohydrazonyl chloride, m.p. 126—128° (8·4 g, 72%), precipitated. On recrystallization from acetone the chloride had m.p. 129—130° (Found: C, 68·7; H, 5·6; N, 11·7. $C_{14}H_{13}ClN_2$ requires C, 68·85; H, 5·3; N, 11·5%). *Phenyl N-phenyl-p-toluohydrazonate* was then prepared from the chloride by Method B (above) and had m.p. 189° (Found: C, 79·7; H, 6·35; N, 9·5. $C_{20}H_{18}N_2O$ requires C, 79·5; H, 6·0; N, 9·3%). *Phenyl N-(phenyl)-p-chlorobenzohydrazonate* was also prepared by this route and had m.p. 110° (Found: C, 70·3; H, 4·8; N, 8·9. $C_{19}H_{15}ClN_2O$ requires C, 70·6; H, 4·6; N, 8·7%).

Phenyl N-(p-Nitrophenyl)benzohydrazonate.—Benzaldehyde *p*-nitrophenylhydrazone (4·6 g, 0·02 mol) was dissolved in acetic acid (80 ml) and bromine (1·1 ml) also dissolved in acetic acid (10 ml) was added dropwise over 2 h. The precipitated *N*-(*p*-nitrophenyl)benzohydrazonyl bromide was filtered off and washed with ice-cold water and then with ether. Recrystallization from anhydrous acetic acid gave the hydrazonyl bromide, m.p. 189—191° (lit.,[40] m.p. 191°). The hydrazonate was prepared from this using Method B above and had m.p. 175—178° (Found: C, 68·3; H, 4·7; N, 12·55. $C_{19}H_{15}N_3O_3$ requires C, 68·5; H, 4·5; N, 12·55%). The following substituted *aryl N-(p-nitrophenyl)benzohydrazonates* were similarly prepared: *p*-Br, m.p. 234—237° (Found: C, 55·0; H, 3·4; N, 10·2. $C_{19}H_{14}BrN_3O_3$ requires C, 55·3; H, 3·4; N, 10·2%); *m*-Br, 174—177° (Found: C, 55·1; H, 3·3; N, 10·2%); *p*-Me, 228—231° (Found: C, 68·6; H, 4·85; N, 11·85. $C_{20}H_{17}N_3O_3$ requires C, 69·2; H, 4·9; N, 12·1%); *p*-NO_2, 224—226° (Found: C, 60·1; H, 3·85; N, 14·8. $C_{19}H_{14}N_4O_5$ requires C, 60·3; H, 3·7; N, 14·8%).

Phenyl *N*-(*p*-nitrophenyl)-*p*-nitrobenzohydrazonate was similarly prepared by Method B from sodium phenoxide and *N*-(*p*-nitrophenyl)-*p*-nitrobenzohydrazonyl bromide.[40] The *hydrazonate* had m.p. 278—280° (Found: C, 59·4; H, 3·9; N, 14·1. $C_{19}H_{14}N_4O_5$ requires C, 60·3; H, 3·7; N, 14·8%).

Phenyl N-(p-Tolyl)benzohydrazonate.—Benzoyl chloride (14·1 g, 0·10 mol) was added dropwise over 1 h at room temperature to a vigorously stirred solution of *p*-tolylhydrazine hydrochloride (15·1 g, 0·10 mol) in dry pyridine (150 ml). The mixture was added to crushed ice and then set aside for 4 h. The *N*-(*p*-tolyl)benzohydrazide which precipitated was filtered off, m.p. 143—146° (20·5 g, 91·5%), m.p. 146—147° (from ethanol). The hydrazide (11·3 g, 50 mmol) and phosphorus pentachloride (12·3 g, 60 mmol) were refluxed in dry ether (150 ml) for 18 h. The solution was worked up as described above in the

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

preparation of *N*-phenyl-*p*-toluohydrazonyl chloride, to give N-(p-*tolyl*)*benzohydrazonyl chloride*, m.p. 126—131° (8·6 g, 74%), m.p. 131—132° (from acetone) (Found: C, 68·9; H, 5·6; N, 11·7. $C_{14}H_{13}ClN_2$ requires C, 68·85; H, 5·4; N, 1·5%). Reaction of the hydrazonyl chloride with phenol by Method B gave *phenyl* N-(p-*tolyl*)*benzohydrazonate*, m.p. 186° (Found: C, 79·4; H, 6·3; N, 9·6. $C_{20}H_{18}N_2O$ requires C, 79·5; H, 5·0; N, 9·3%). The following hydrazonates were similarly prepared: *phenyl* N-(p-*chlorophenyl*)-*benzohydrazonate*, m.p. 147° (Found: C, 71·2; H, 4·9; N, 8·4. $C_{19}H_{15}ClN_2O$ requires C, 70·6; H, 4·6; N, 8·7%); *phenyl* N-(p-*tolyl*)-p-*toluohydrazonate*, m.p. 90° (Found: C, 79·6; H, 7·35; N, 8·3. $C_{21}H_{20}N_2O$ requires C, 79·7; H, 6·3; N, 8·9%).

Phenyl N-*phenyl*(*thiobenzohydrazonate*).—Sodium hydride (0·48 g, 10 mmol) was added slowly with stirring to thiophenol (1·10 g, 10 mmol) in dry benzene (50 ml). The sodium thiophenoxide suspension was added over 1 h with vigorous stirring to a solution of *N*-phenylbenzohydrazonyl chloride (2·3 g, 10 mmol) in dry benzene (150 ml); the reaction was protected from moisture throughout. Sodium chloride (0·35 g, 60%) was filtered off and the solvent evaporated at reduced pressure to give a red oil. On work-up with light petroleum (b.p. 80—100°) a yellow solid was obtained from the oil, m.p. 68—71° (1·50 g, 49%). On recrystallization from light petroleum (twice) the *thiohydrazonate* had m.p. 70—71° (Found: C, 75·0; H, 5·45; N, 8·9; S, 10·9. $C_{19}H_{16}N_2S$ requires C, 75·0; H, 5·3; N, 9·2; S. 10·5%).

NN′-*Diphenylbenzamidrazone*.— *N*-Phenylbenzohydrazonyl chloride (0·92 g, 4 mmol) and aniline (0·75 g, 8 mmol) were thoroughly mixed in the absence of a solvent and heated to 100° for 10 min. The red semi-solid which slowly formed was washed repeatedly with water (to remove aniline hydrochloride) and filtered off. The residue was washed with ether (10 ml) and then recrystallized from 95% ethanol (twice) to give the *amidrazone*, m.p. 171—172° (Found: C, 79·9; H, 6·3; N, 14·6. $C_{19}H_{17}N_3$ requires C, 79·4; H, 5·9; N, 14·6%). N-*Methyl*-N-*phenylbenzamide phenylhydrazone*, prepared by a similar method had m.p. 140—141° (Found: C, 78·8; H, 6·4; N, 14·1. $C_{20}H_{19}N_3$ requires C, 79·7; H, 6·2; N, 14·1%).

NN′-*Diphenylbenzohydrazide*.—Hydrazobenzene (1·84 g, 10 mmol) which had been recrystallized three times from ethanol, was dissolved in dry pyridine (50 ml) and benzoyl chloride was added to the stirred solution over 1 h at room temperature. The mixture was added to crushed ice and set aside for 4 h. The solid material which separated (2·03 g, 70%), m.p. 98—102°, gave, on recrystallization from ethanol, the *hydrazide*, m.p. 102—104° (Found: C, 78·7; H, 5·7; N, 9·7. $C_{19}H_{16}N_2O$ requires C, 78·9; H, 5·9; N, 9·7%).

N′N′-*Diphenylbenzohydrazide*.— NN-Diphenylhydrazine hydrochloride (1·1 g, 5 mmol) was dissolved (at 50°) in water (50 ml). Sodium hydroxide (0·20 g, 5 mmol) was added and the solution was stirred at ambient temperature for 30 min. The solution was then extracted with ether (3 × 100 ml) and the dried extracts evaporated to give the free hydrazine as a yellow oil which was dried *in vacuo* (over calcium carbonate). The oil was dissolved in pyridine (50 ml) and benzoyl chloride (0·70 g, 5 mmol) was added and the *hydrazide* was obtained (as detailed above), m.p. 190—191° (from 95% ethanol) (Found: C, 79·3; H, 5·3; N, 9·6%).

Rearrangements.—*Method A*. Phenyl *N*-phenylbenzohydrazonate (0·28 g, 1 mmol) was heated in a Pyrex test tube at 220° for 10 min (oil-bath). When cooled to room temperature the rearrangement product *N′N′*-diphenylbenzohydrazide was obtained (0·28 g, virtually quantitative yield), m.p. 186—190°. On recrystallization from ethanol the hydrazide had m.p. 191—192°, and was identical (mixed m.p., spectra) with an authentic sample, prepared as detailed above.

TABLE 3

The *N′N′*-diarylbenzohydrazides (6) [a]

Ar[1]	Ar[2]	Ar[3]	M.p./°C [b]
Ph	*m*-BrC_6H_4	Ph	134—138
Ph	*p*-MeC_6H_4	*p*-MeC_6H_4	186
Ph	*o*-ClC_6H_4	*p*-$NO_2C_6H_4$	197—198
p-BrC_6H_4	*p*-$NO_2C_6H_4$	Ph	114—115
m-BrC_6H_4	*p*-$NO_2C_6H_4$	Ph	95—96
p-MeC_6H_4	*p*-$NO_2C_6H_4$	Ph	92—93
p-$NO_2C_6H_4$	*p*-$NO_2C_6H_4$	Ph	228—231
p-MeC_6H_4	Ph	Ph	209—210
p-ClC_6H_4	Ph	Ph	195—196
p-$NO_2C_6H_4$	Ph	Ph	197—198

[a] See also Table 1 for additional data on hydrazides. [b] In all cases the hydrazides gave acceptable C, H, and N analyses (± 0·3%) and had an i.r. absorption in the region 1640—1670 cm^{-1}; t.l.c. analysis indicated the absence of the isomeric hydrazonate (5).

Method B. Phenyl *N*-phenylbenzohydrazonate (0·29 g, 1 mmol) was dissolved in dry benzene (15 ml) and active manganese dioxide [28] (0·09 g, 1 mmol) was added. The mixture was refluxed for 1 h and then reduced to *ca.* 5 ml by evaporation of the solvent. Inorganic salts were filtered off and the solvent removed *in vacuo* to give *N′N′*-diphenylbenzohydrazide (0·28 g, *ca.* 99%), m.p. 191—192°.

The other hydrazides listed in Tables 1 and 3 were prepared by Method A and/or B, and generally recrystallized from absolute ethanol. The reaction time was usually gauged by testing a sample for the appearance of the carbonyl stretching band at *ca.* 1670 cm^{-1} and using t.l.c. Longer reaction times were in general required when the hydrazonate had electron-withdrawing substituents.

Hydrolysis of N′N′-*Diphenylbenzohydrazide*.—*N′N′*-Diphenylbenzohydrazide (2·88 g, 10 mmol), obtained by thermal rearrangement of phenyl *N*-phenylbenzohydrazonate, was refluxed for 16 h with concentrated hydrochloric acid (2 ml, 12N) in 95% ethanol (50 ml). The solution was evaporated under reduced pressure to *ca.* 5 ml and, on cooling, a solid, m.p. 154—160° (2·01 g, 60%), was obtained. This was identified as *NN*-diphenylhydrazine hydrochloride by comparisons with an authentic sample of the hydrazine and benzylidene derivatives.

Hydrolysis of N-*Phenyl*-N-(p-*nitrophenyl*)*benzohydrazide*.—The hydrazide obtained by rearrangement (Method A) of phenyl *N*-(*p*-nitrophenyl)benzohydrazonate or of *p*-nitrophenyl *N*-phenylbenzohydrazonate was hydrolysed in ethanol–concentrated hydrochloric acid to give *N*-phenyl-*N*-(*p*-nitrophenyl)hydrazine hydrochloride. The hydrazine was identified by conversion into the free base and (a) reaction in dry pyridine with benzoyl chloride to regenerate *N*-phenyl-*N*-(*p*-nitrophenyl)benzohydrazide and (b) formation of a *benzylidene derivative*, m.p. 139—140° (Found: C, 71·2; H, 5·1; N, 13·1. $C_{19}H_{15}N_3O_2$ requires C, 72·0; H, 4·75; N, 13·2%).

Rearrangement of Mixtures of Hydrazonates.—Phenyl *N*-phenylbenzohydrazonate (0·5 g) and *p*-tolyl *N*-*p*-tolylbenzohydrazonate (0·5 g) were intimately mixed and heated

at 200° for 10 min in the absence of solvent. On cooling the mixture of hydrazides was analysed by t.l.c. [on alumina using benzene–n-pentane–triethylamine (15 : 4 : 1) as mobile phase] and showed the presence of *N'N'*-di-*p*-tolylbenzohydrazide and *NN*-diphenylbenzohydrazide. No cross-over product, *N'*-phenyl-*N'*-(*p*-tolyl)benzohydrazide was detected. Similarly, rearrangement of a mixture of *p*-tolyl *N*-phenylbenzohydrazonate and phenyl *N*-(*p*-tolyl)-benzohydrazonate gave a single product, *N'*-phenyl-*N'*-*p*-(tolyl)benzohydrazide. T.l.c. analysis indicated in a control experiment that the possible cross-over products, *N'N'*-diphenylbenzohydrazide and *N'N'*-di-*p*-tolylbenzohydrazide would have been detected if present at concentrations $\geqslant 5\%$. The absence of cross-over was also indicated using several other pairs of hydrazonates; in each case the product mixture was analysed by t.l.c. Similar results were obtained when the mixed hydrazonates were refluxed for 1 h in benzene in the presence of an equimolar quantity of activated manganese dioxide.

Kinetic Experiments.—(a) *In dioxan–water.* 4 : 1 (v/v) Dioxan–water was prepared at 25°. The dioxan used was AnalaR grade, used without further purification; the water was deionized and distilled from potassium permanganate. The substrate was made up in this solvent at a concentration (10^{-4}—10^{-5}M) suitable for u.v. analysis and then distributed amongst ampoules (10 at a minimum). The ampoules were heated at 97° and the u.v. spectra (280—400 nm) of the contents were recorded (on cooling to 25°) at suitable time intervals (Figure 1). The first point was usually taken after *ca.* 5 min at 97° to allow temperature equilibration. Under these conditions the initial period of inhibition (see Figure 3) did not interfere and reasonable pseudo-first-order plots of log (O.D.$_t$ −O.D.$_\infty$) *vs.* *t* were obtained. The rate constants measured by this method were reproducible within ±5%; however larger variations were obtained when different batches of dioxan–water were used.

(b) *In* 95% *ethanol.* The 95% ethanol used was a redistilled middle fraction (*ca.* 60% of total). The substrate was made up at *ca.* 10^{-4}—10^{-5}M in this solvent and the decrease in optical density at 340 nm was continuously monitored at 75° using a Unicam SP 1800 u.v. spectrophotometer fitted with an AR25 recorder. In the absence of added catalysts the hydrazonate was essentially stable in the purified solvent, but reaction was accelerated by the addition of small quantities (10^{-4}M) of hydrochloric acid (from ' Volucon ' ampoules) or radical initiators (see text). In the unredistilled solvent rearrangement also occurred under these conditions, possibly due to the presence of small quantities of impurities which act as radical initiators.

[3/487 *Received, 5th March,* 1973]