

560. *Mechanism of Benzidine and Semidine Rearrangements.*
Part XV.¹ A Collective Discussion.

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The theoretical position of the problem of mechanism presented by the benzidine and semidine rearrangements is examined in view of recent observations, including those recorded in Parts I—XIV.¹ The main groups of observations are summarised. They relate to the kinetics and products of rearrangement, the products in correlation with kinetics where possible, and both kinetics and products in relation to substrate structure and environmental conditions. Of the three propounded theories of the rearrangement which treat the stereochemical side of the problem seriously, *viz.*, the polar-transition-state, the π -complex, and the caged-dissociation theories, the first alone is consistent with the overall observational picture. The new observations allow this theory to be kinetically and stereochemically particularized.

THE term "benzidine rearrangement" will usually be employed to embrace the conversions of aromatic hydrazo-compounds to both diaminobiaryls (benzidines, diphenylines, *ortho*-benzidines) and aminodiarylamines (*ortho*- and *para*-semidines). Occasionally, but only where the context so indicates, the same term will be used in more restricted senses, as in the title to cover conversions to diaminobiaryls only, or elsewhere to comprise conversions to benzidines, that is, to 4,4'-diaminobiaryls only.

¹ Parts I—VII, *J.*, 1962, 2386—2444; Parts VIII—XI, 3294—3318; Parts XII—XIV, the three preceding Papers.

(1) *Background*.—We think the present a suitable time to assess the position, reached after the first fourteen Parts of this series,¹ in the 60-year-old problem of the mechanism of the benzidine rearrangement. It is one of the aromatic rearrangements which do not proceed by a combination of standard, independently known, reactions of the side-group and of the nucleus.

Tichwinsky's and Stieglitz's theories of the benzidine rearrangement, which were pre-electronic equivalents of rearrangement by homolytic and heterolytic dissociation, respectively, were both promulgated in 1903. In both, the concept of dissociation was adopted as the only then obvious means of avoiding a formidable stereochemical difficulty. Nevertheless, as summarised in Part IV,² the succeeding 30 years saw a steady accumulation of evidence against dissociation, and, after 1933, when a critical test by the non-crossing of products was recorded, which has been well-confirmed since (cf. Parts IV² and XIV¹), the idea was dropped. It then became accepted that the benzidine rearrangement was intramolecular, despite the fact that so drastic a convolution of the molecular framework implied configurations along the reaction co-ordinate completely unlike those of any normal molecule. The second 30-year period falls into two parts. Up to 1950, the contributions to the problem were mainly theoretical; only a few significant new facts came to light. Since 1950, the main activity has been the assembling of new observations. It is essentially in consequence of this observational development that re-appraisal of the theoretical position is now needed, as is our purpose here. And so we next recall the main theoretical suggestions which have to be further considered.

(2) *Theories of Mechanism*.—Current theories of the benzidine rearrangement bring out the special character of that reaction, which separates it mechanistically from the great majority of organic reactions, and which has, indeed, been a serious barrier to the elucidation of its mechanism. For most reactions, it is assumed, by generalisation of a treatment first developed by London, that the exchanging bonds in a transition state are describable to a useful approximation as resonance hybrids of those bonds of the initial and final states that become exchanged in the reaction. The theories that we shall consider have recognised that the benzidine rearrangement cannot conform to that condition. Whatever details are to be filled in, it must be assumed that the bonding in the transient configurations along the reaction co-ordinate, and, in particular, in the transition state, is too radically different from the bonding in the initial and final states to allow the transient bonding to be described by quantal mixings of end-state bondings. With this loss of the normal guide-lines, it is not surprising that quite a variety of assumptions have been made about the nature of the transient bonding.

One type of theory is that which was incepted by Hughes and Ingold³ in 1941, and has been modified since, notably by incorporation of a suggestion by Hammick and Mason⁴ in 1946. This theory assumes highly polar bonding along the reaction co-ordinate, and a transition state containing at least two bonds, which are mainly, though not wholly, electrovalent. This circumstance allows the bonds much greater lengths than are normal to bonds, and (as Hammick and Mason added) much lower bending force-constants, and hence very different angles from those of ordinary bonds. These geometrical and mechanical characteristics of the bonds permit shape-changes along the reaction co-ordinate which can be drastic enough, and yet energetically easy enough, to fulfil without difficulty the drastic stereochemical demands of the rearrangement.

In 1945, Dewar⁵ proposed a theory, which has since been modified in detail, but is

² Banthorpe, *J.*, 1962, 2413.

³ Hughes and Ingold, (a) *J.*, 1941, 608; (b) 1950, 1638; (c) Ingold, in "The Transition State," *Chem. Soc. Special Publ.*, No. 16, 1962, p. 118.

⁴ (a) Hammick and Mason, *J.*, 1946, 220; (b) Hammick and Munro, *ibid.*, 1950, 2049.

⁵ Dewar, (a) *Nature*, 1945, 176, 784; (b) *J.*, 1946, 406; (c) *ibid.*, p. 777; (d) "Electronic Theory of Organic Chemistry," Clarendon Press, Oxford, 1949, p. 233; (e) *Bull. Soc. chim. France*, 1951, 71C; (f) *Ann. Reports*, 1951, 48, 126; (g) "Theoretical Organic Chemistry. Kekulé Symposium," Butterworths, London, 1959, p. 195.

distinguished by the feature that rearrangement is assumed to go through a protonated " π -complex." This is a specialised hypothetical intermediate in which the original N-N bond is replaced by a delocalised covalency, called a " π -bond," between the aromatic rings. The rings are thus held in parallel planes, though with the possibility of relative rotation. Products follow by replacement of the π -bond by a localised interatomic bond.

One other theory deserves discussion, inasmuch as it also treats the stereochemical challenge seriously.* It assumes a homolytic splitting of the protonated hydrazo-molecule into fragments, which are structurally independent radical intermediates, but are restrained from kinetic independence by a solvent cage. This idea has been mentioned more than once, but seriously advocated only recently. An evident objection to it is that it would be difficult to understand the absence of attack on the walls of the cage, indeed, on those of any of a variety of cages; for benzidine rearrangements have been conducted in many solvents, no characteristic fragment of any of which has ever appeared in combination among the rearrangement products. A further objection is that sensitive methods for the detection of radical intermediates have failed to disclose any (see Addendum to this Paper). Dewar has criticised^{5f,g} the cage theory on the ground that the internal distribution of reactivity in a particular structurally independent fragment should be largely independent of its origin, whereas the recorded data on products of benzidine rearrangements show that nothing like that can be true. Večera and his co-workers have, however, recently advocated the idea of a preliminary splitting of the doubly protonated hydrazo-molecule into two radical-ions in a solvent cage;⁸ however, it is difficult to understand how their data lead to such a particular conclusion. They measured the variation in the rate of acid rearrangement of hydrazobenzene, when the Hammett acidity, and the solvent, were changed together, and failed to establish a quantitative correlation of the measured rates with the Hammett acidity alone. They also studied product composition as a function of the solvent. Aniline radical-ions, as intermediates, have been made improbable by Adams and his co-workers.⁹ They showed by several mutually supporting techniques, including polarography, electron spin resonance spectroscopy, spectrophotometry, and isotopic-tracer methods, that, when *NN*-dimethylaniline is anodically oxidised to give *NNN'*-tetramethylbenzidine as main product, each dimethylaniline molecule that loses any electrons at all loses two at once, thus cutting out the radical-ion stage of oxidation, to give the doubly charged cation directly; this then reacts with a neutral dimethylaniline molecule to give the benzidine. Such interaction between a doubly charged and a neutral aromatic unit is exactly what we assume in the acid rearrangement of hydrazobenzene,^{3b,c} (cf. Section 15).

All three of these theories are to be further discussed, and we shall refer to them as the "polar-transition-state," the " π -complex," and the "caged-dissociation" theories.

Up to 1950, all theories assumed acid catalysis by one added proton, notwithstanding a record of 1904 by van Loon¹⁰ to the effect that the rearrangement of hydrazobenzene is of second-order in hydrogen ions. In 1950, Hammond and Shine¹¹ recorded the same finding, and thereafter theories were modified, as they easily could be, to accommodate the second added proton.

(3) *Kinetic Forms of Acid-catalytic Rearrangement.*—Since 1950, a number of investigators

* Robinson's theory does not do so; in fact, he explicitly brushes it aside.⁶ The idea that 2,2'-linking without 2,2'-hydrogen-loss might produce an intermediate for all forms of rearranged linking⁷ does meet the stereochemical challenge; however, it was never developed into a theory because it received no support from studies of hydrogen-isotope effects on rates and products (cf. Section 10), and because it seemed difficult thus to accommodate all that we knew about products in their dependence on structure (cf. Sections 12—14).

⁶ Robinson, *J.*, 1941, 220.

⁷ Brownstein, Bunton, and Hughes, *Chem. and Ind.*, 1956, 981.

⁸ Večera, Synek, and Sterba, *Coll. Czech. Chem. Comm.*, 1960, **25**, 1992.

⁹ (a) Mizoguchi and Adams, *J. Amer. Chem. Soc.*, 1962, **84**, 2058; (b) Galus and Adams, *ibid.*, p. 2061; (c) Galus, White, Rowland, and Adams, *ibid.*, p. 2065.

¹⁰ van Loon, *Rec. Trav. chim.*, 1904, **23**, 62.

¹¹ Hammond and Shine, *J. Amer. Chem. Soc.*, 1950, **72**, 220.

have been concerned to generalise the Loon–Hammond–Shine finding to various substituted hydrazobenzenes and various solvents.^{12–15} In the course of this work, Carlin and Odioso^{12b} encountered the anomaly that in their conditions the rearrangement of 2,2'-dimethylhydrazobenzene had an order in acid, not of 2, but of 1.6. The search now became one for the limits of validity for the Loon–Hammett–Shine kinetics. Carlin and his co-workers sought further examples of a similar anomaly, examining with particular care 3,3'- and 4,4'-dimethylhydrazobenzene;^{12c,d} however, no other such case was found. Blackadder and Hinshelwood¹⁴ interpreted Carlin and Odioso's anomalous result, as we did when incepting the present work (cf. Parts I and V¹), on the basis of an assumption that a second acid-catalysed mechanism of benzidine rearrangement, one linear in hydrogen ions, existed, though it had not up to then been isolated; and we took up the task of trying to isolate it.

Our approach was based on the polar-transition-state theory, which did suggest a possible answer to the following inescapable first question. Granted that the Carlin–Odioso anomaly was to appear somewhere, why should it do so in just that one example, out of all the examples that had been examined prior to our work? The suggested answer was that the *ortho*-methyl substituent has the combination of properties, which it shares with only a few other aromatic substituents, that it both weakens an aniline base, and donates electrons to the benzenoid ring. By reducing the basicity of a hydrazo-nitrogen atom, an *ortho*-methyl substituent would increase the electron affinity there built up by protonation; and, in Carlin and Odioso's example, the other *ortho*-methyl group, by supplying electrons to, and through, its benzene ring, would facilitate heterolytic displacement of the N–N bond-electrons towards the first-added proton. If this combination of effects were strong enough, so we might suppose, one added proton would suffice to determine the leading heterolysis of the rearrangement.

One could think of a few other substituents which might act like *ortho*-methyl, for reasons connected, in some cases mainly with one or the other of the assumed two mutually complementary properties, but in other cases with both. When improvements in *both* properties are to be expected on replacing one substituent by another, then qualitative prediction as to relative kinetic effects may be attempted. Relatively to *ortho*-methyl, improvements in both properties are expected in the benzo-substituent of the 2-naphthyl group, and still greater improvements in both are expected in the benzo-substituent of the 1-naphthyl group. The groups 1-naphthyl, 2-naphthyl, *o*-tolyl, and phenyl should form a monotonic series of groups in diminishing order of importance in that combination of properties which is thought to be significant for rearrangement activated by only one added proton. As will be seen below, we know something of this series from observation; but the series could be extended theoretically where no observational answers are yet available. For instance, 2-biphenyl should fit in between 1-naphthyl and *o*-tolyl, as 4-biphenyl should between 2-naphthyl and *o*-tolyl, and also between 2-biphenyl and *o*-tolyl. The anisyl groups are nearly as easy subjects for prediction, but it would be unfair to cite them, because we know the answers through unpublished observations.*

* A Paper by Shine and Chamness has just appeared,¹⁶ which shows that the rearrangement of 4,4'-divinylhydrazobenzene in aqueous ethanol is of first-order in acid. In the structural features which we think relevant to the kinetic form of rearrangement, this hydrazo-compound is analogous to the 2,2'-hydrizonaphthalene. A preliminary announcement has been made of kinetics corresponding to the one-proton mechanism in the rearrangement of 3,3'-diaminohydrazobenzene.¹⁷ This structural effect is consistent with, but could not be predicted by, the argument in the text. The same is true of a recent example of fractional-order kinetics,¹⁸ to which reference is made below.

¹² (a) Carlin, Nelb, and Odioso, *J. Amer. Chem. Soc.*, 1951, **73**, 1002; (b) Carlin and Odioso, *ibid.*, 1953, **75**, 100; (c) Carlin and Odioso, *ibid.*, p. 2345; (d) Carlin and Wich, *ibid.*, 1958, **80**, 4023.

¹³ Croce and Gettler, *J. Amer. Chem. Soc.*, 1953, **75**, 874.

¹⁴ Blackadder and Hinshelwood, *J.*, 1957, 2898.

¹⁵ Bunton, Ingold, and Mhala, *J.*, 1957, 1906.

¹⁶ Shine and Chamness, *J. Org. Chem.*, 1963, **28**, 1232.

¹⁷ Hammond and Clovis, *Tetrahedron Letters*, 1962, 945.

¹⁸ White and Preisman, *Chem. and Ind.*, 1961, 175.

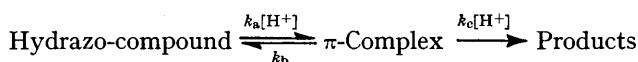
Our first kinetic investigation, that of the acid-rearrangement of 1,1'-hydrazonaphthalene, showed that in aqueous dioxan this reaction follows kinetics completely linear in hydrogen ions (Part I¹). When the 1-naphthyl groups in this substrate were successively replaced by groups further to the right in the theoretical monotonic series written above, one passed, through intermediate and non-integral kinetic forms, finally to the second limiting kinetic form, quadratic in hydrogen ions, characteristic of the rearrangement of hydrazobenzene itself (Parts II—VIII¹).

It was important to discover how the two limiting kinetic forms could be embraced in a comprehensive kinetic scheme which would take quantitative account of the transitional kinetic situations. Blackadder and Hinshelwood, in their explanation of Carlin and Odioso's anomalous kinetic result, had assumed that two integral kinetic orders would represent two independent catalytic mechanisms, which, in Carlin and Odioso's case, were running concurrently. This implies that, in a reaction of apparently fractional-order in acid, the component rates of integral-order combine by simple addition, as in equation (1):

$$-(d[\text{Hz}]/dt)/[\text{Hz}] = k_2[\text{H}^+] + k_3[\text{H}^+]^2 \quad (1)$$

where k_2 and k_3 are second- and third-order rate constants, respectively. From this it follows that, towards limits of high and low acidity, the kinetic order in acid will converge on two and one, respectively.

Dewar took a different view.^{5f,g} He envisaged, not two mechanisms, but one mechanism of two steps, in which functions for two protons had to be found, which would allow one proton, without losing its assigned chemical function, occasionally to disappear from kinetic significance. He allotted one proton to each step, that is, one to the formation of his π -complex, and one to its conversion to products, as in the scheme:



where k_a and k_c are second-order rate constants, and k_b is a first-order constant. According to whether the first or the second forward step is wholly rate-controlling, the overall order in acid will be one or two. It was assumed that, in a reaction of intermediate apparent order in acid, rate control is comparably shared between the steps. From this it follows, by the stationary-state principle, that the integral-order rates, which would obtain if one step or the other had exclusive control of the rate, combine to produce mixed-order kinetics, not additively, but "harmonically," that is, by addition of their reciprocals to give the reciprocal of the mixed-order rate, in accordance with equation (2):

$$\frac{1}{-(d[\text{Hz}]/dt)/[\text{Hz}]} = \frac{1}{k_a[\text{H}^+]} + \frac{1}{Kk_c[\text{H}^+]^2} \quad (2)$$

where $K = k_a/k_b$. Equation (2) is the equivalent of an equation given by Dewar.^{5g} It is obvious that some of the consequences of equation (2) will be qualitative opposites to those of equation (1), and, in particular, that, towards the limits of high and low acidity, the kinetic order in acid will converge on one and two, respectively.

The result that the rearrangement of 1,1'-hydrazonaphthalene is of first order in hydrogen ions in itself contradicts the π -complex theory of rearrangement. π -Complexes involving the naphthalene molecule or residue, together with an electron-accepting or -donating second component, are always much more stable than corresponding π -complexes involving the benzene molecule or residue; this is the universal rule observationally, and it is well understood theoretically. It is thus to be expected that the naphthalene π -complex will be more stable than the benzene π -complex to all decompositions that involve the breaking of the π -bond. If a second proton is needed, as in Dewar's theory it is, to accomplish the breakdown of the π -complex intermediate from hydrazobenzene, as

the slow step of rearrangement of hydrazobenzene, a second proton must be needed *a fortiori* to secure breakdown of what should be the much more stable π -complex from 1,1'-hydrazonaphthalene, in the slow step of rearrangement of 1,1'-hydrazonaphthalene. As the rearrangement of hydrazobenzene is of second-order in acid, that of 1,1'-hydrazonaphthalene should *a fortiori* be of second-order in acid, contrary to the observations.

The steps by which substrate structure was changed, so as to pass by small degrees from the linear acid-dependence of the rearrangement of 1,1'-hydrazonaphthalene to the quadratic acid-dependence of that of hydrazobenzene, are shown in Table 1. Transitional kinetics were manifest in four of the five intermediate cases, thus used to form a bridge between the kinetic extremes. Another case of transitional kinetics, that of the rearrangement of *N*-methylhydrazobenzene, has been described by White and Preisman.¹⁸ In four cases, including this last, the manner of combination of the limiting integral-order rates, in the ranges of acidity in which the order in acid is markedly non-integral, has been established in detail. A non-integral order in acid cannot, of course, be represented by any firm figure, because the order changes with the acidity. Carlin and Odioso's figure, 1.6, for the order in acid of the rearrangement of 2,2'-dimethylhydrazobenzene, applies only to the particular narrow range of acidities which they employed. In all the four investigated cases, it was shown that the apparent order in acid rises with the acidity, in qualitative disagreement with equation (2), and in quantitative agreement with equation (1).

TABLE 1.

Benzidine rearrangements in aqueous dioxan: substrate structure and kinetic order in acid, relative to the group sequence 1-C₁₀H₇, 2-C₁₀H₇, 2-MeC₆H₄, Ph.

No.	R·NH·NH·R'		Kinetic order in acid		Ref. or Part No. ¹
	R	R'	Low acid	High acid	
(1)	1-C ₁₀ H ₇	1-C ₁₀ H ₇	1.0	1.0	I
(2)	1-C ₁₀ H ₇	2-C ₁₀ H ₇	1.0	1.0	II
(3)	2-C ₁₀ H ₇	2-C ₁₀ H ₇	1.0	ca. 1.2	III
(4)	1-C ₁₀ H ₇	Ph	1.0	ca. 2.0	V *
(5)	2-C ₁₀ H ₇	Ph	ca. 1.1	ca. 2.0	VI *
(6)	2-MeC ₆ H ₄	2-MeC ₆ H ₄	ca. 1.3	ca. 2.0	12b, VII *
(7)	Ph	Ph	2.0	2.0	10, 11, 12a, 14, 15, VIII
(8)	4-MeC ₆ H ₄	4-MeC ₆ H ₄	2.0	2.0	15, 12d

* Quantitative agreement with equation (1) was established in these examples.

The π -complex theory, which leads to equation (2),* is thus inconsistent with these detailed studies of transitional kinetics. It is also inconsistent with some other matters of kinetic form to which reference is made in Table 1. When Dewar adjusted his theory to accommodate the second catalytic proton,^{5f} he pointed to the consequence that, whereas benzidine formation had been shown to be quadratic in acid, semidine formation should prove to be linear, because, in terms of the theory, non-proton-assisted rotation of the first-formed π -complex would have to be faster than the proton-assisted breakdown of this complex. At that time, the kinetics of semidine formation were not known; however, they were determined soon afterwards [example No. (8) in Table 1], and the order in acid proved to be two,^{15,12d} contrary to prediction.†

Actually, an analogous discrepancy existed between the consequences of π -complex theory and facts, relating to example no. 7 in Table 1, which were well known at the time of revision of the theory.^{5f} For Dewar's deductions concerning the kinetics of semidine formation apply equally to diphenylene formation; in terms of the theory, a diphenylene, equally with a semidine, is formed through a rotated π -complex. It follows, since the acid

* So does Carlin and Odioso's idea^{12b} that protonation in the initial state causes order-in-acid to fall below two. But this suggestion has already been criticised by Dewar.^{5f}

† A communication by Shine and Chamness has just appeared, which establishes the same point in the example of 4,4'-di-*t*-butylhydrazobenzene.¹⁹

¹⁹ Shine and Chamness, *Tetrahedron Letters*, 1963, 641.

rearrangement of hydrazobenzene gives 73% of benzidine and 27% of diphenylene, (a) that the order in acid of the overall rearrangement should not be two, and (b) that the ratio in which the two products are formed should not be independent of the acidity. It had been shown, on the contrary, that the order in acid is accurately two,¹¹ and that the product composition is independent of the acidity.^{12a}

We next consider the bearing of the kinetic results of Table I on the theory of homolysis in a solvent cage. The first point to be made here is that this theory is inconsistent with the concurrence of the one-proton and two-proton mechanisms. The concurrence shows generally that the first-added proton is much more important than the second as an activator of the hydrazo-system for rearrangements; for, once the first proton has been accepted, the uptake of a second further assists activation, if at all, only to about the extent of a mild constitutional modification, such as the introduction of *ortho*-methyl or benzo-substituents. It is, on the contrary, characteristic of the caged-dissociation theory that the second-added proton should be considered as the main requirement of the mechanism, because it not only restores the electrical symmetry favouring homolysis (*i.e.*, weakens the bond by destroying ionic resonance energy—Pauling), but also creates the adjacent-charge repulsion desirable for homolytic separation of the two radical-ions (though why two ions of like charge should stay in the same solvent cage is not explained). The first-added proton could, by itself, produce no such good causes for the homolysis; thus, one can well understand why the formerly supposed indispensability of the second-added proton was claimed as an important argument in favour of the caged-dissociation theory. That theory is incompatible with one-proton rearrangement *per se*. It is incompatible *a fortiori* with that easy concurrence of the one-proton and two-proton mechanisms, which shows that first-added proton goes either all the way, or nearly all the way, in activating the system for rearrangement.

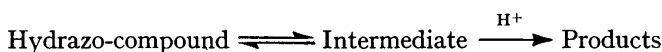
If we should try to avoid these difficulties by proposing heterolytic bond-changes in the one-proton mechanism but homolytic bond-changes in the two-proton mechanism, then other difficulties would arise, one of which is already apparent in Table I. This is that when, starting from a symmetrical hydrazo-compound, we effect first a mono-substitution and then a symmetrical di-substitution by a second use of the same substituent, we observe two successive shifts of mechanism in the same direction. According to the suggestion being examined, the shifts should be in opposite directions. Other difficulties arise from the generally parallel behaviour of the two mechanisms with respect to solvent and salt effects (Sections 6 and 7). According to the same suggestion, the polar solvent and salt effects should be very different in the two mechanisms. Yet another group of difficulties arises from the study of product compositions as a function of kinetic form (Section 13); the products are the same in the one-proton and two-proton mechanisms, except for differences that can be understood without the assumption of a fundamental difference of character in the bond changes. It should be said that no suggestion of such a difference has appeared in the literature.

The more positive teaching of Table I is that the observations on kinetic form there summarised support the polar-transition-state theory of the benzidine rearrangement. This theory does make the first-added proton the more important activator of the rearranging system. For the mechanism depends on N-N heterolysis, in preparation for which the first proton produces a desirable electrical dissymmetry. The second proton performs the two largely countervailing tasks of destroying this dissymmetry, but creating adjacent-charge repulsion. Thus, the second proton acts only through the difference of these opposing effects, and, where it takes any part at all, is only the minor contributor to the activation of the system. In summary, the two-proton mechanism has the role of a minor modification of the one-proton mechanism. Moreover, the structural circumstances, as far as we know them, in which the second proton is or is not useful, are in good agreement with the predictions described, which were based on an assumed N-N heterolysis, leading to the replacement of a covalent by a largely electrovalent mode of linking between

the two aromatic moieties of the hydrazo-structure. Finally, all these relations should, according to that theory, be, and, as far as we know, they are, quite independent of whether the product of rearrangement is to be a benzidine, a diphenylene, or an *ortho*-semidine.

(4) *Kinetics of the Non-catalytic Rearrangements.*—The main theoretical question concerning non-catalytic (so-called thermal) benzidine rearrangements (Parts XII—XIV¹) is that of whether their mechanism belongs to the same family of mechanisms as that of the two acid-catalysed mechanisms, so depending, according to the polar-transition-state theory, on the heterolysis of the N–N bond, and the development of polar bonds. We shall conclude, largely on the evidence of kinetic isotope effects in non-catalytic rearrangement (Section 11), and on that of product compositions (Section 13), that the non-catalytic mechanism in polar solvents probably does belong to the same family as do the two acid-catalytic mechanisms.

As to kinetics, the investigated examples of the non-catalytic reaction are of first-order in substrate both in hydroxylic and non-hydroxylic polar solvents^{20a,b} (Part XII¹). The fact that these reactions are so slow, requiring temperatures of investigation raised by about 100° above those convenient for kinetic study of the corresponding acid-catalytic rearrangements, although it precludes a detailed study of kinetics transitional between the no-proton and the one-proton mechanisms, does of itself answer the question as to how the integral-order rates corresponding to these two mechanisms would combine to produce a mixed-order rate, if the conditions for mixed-order kinetics could be set up. Obviously, the integral-order rates could not combine as the scheme:



would demand, by addition of their reciprocals to give the reciprocal of the mixed-order rate, in analogy with equation (2) (p. 2868), because, if that happened, one would not observe acid catalysis at higher acidities than the extremely low ones which would be required for the observation of transitional kinetics. It thus seems an inevitable conclusion that the integral-order rates of the no-proton and one-proton mechanisms combine by direct addition, in analogy with equation (1) (p. 2868), and in accordance with the idea that the no-proton and one-proton mechanisms, like the one- and two-proton mechanisms, represent independent parallel routes of rearrangement.

It is consistent with our previous conclusions that, in the acid-catalysed reactions, the first-added proton, because it produced electrical dissymmetry, is the dominating, when not the exclusive, protonic activator of the rearranging system, and that to deny its access, as it is denied in the no-proton mechanism, will greatly impede the N–N heterolysis necessary to initiate the electrovalent binding assumed in the polar-transition-state theory. Thus we can understand the relatively low non-catalysed rates. There is no countervailing factor in operation when electrical dissymmetry is precluded by the withholding of the proton, as there is when it becomes levelled out by the supply of a second proton. Hence we can see a reason, in the light of the polar-transition-state theory, why somewhat large kinetic and general differences between the no-proton and one-proton forms of rearrangement contrast with the relatively small differences previously found (Parts I—VIII¹) between the one-proton and the two-proton mechanisms of rearrangement (cf. Table 1).

(5) *Structural Effects on Rearrangement Rate.*—A number of rate constants of rearrangement of hydrazo-compounds by the two-proton mechanism (k_3 of equation 1, p. 2868) in “60%” aqueous dioxan are assembled in the fourth column of the upper part of Table 2. Although these rate constants are not completely uniform with respect to salt conditions, they are sufficiently nearly so to allow validity to the broad comparisons we shall make between the substrates.

²⁰ (a) Shine, *J. Amer. Chem. Soc.*, 1956, **78**, 4807; (b) Shine and Trisler, *ibid.*, 1960, **82**, 4052; (c) Shine, Huang, and Snell, *J. Org. Chem.*, 1961, **26**, 380.

The literature contains many other rate constants, recorded as k_3 values, for the rearrangements of other hydrazo-compounds, or of the same hydrazo-compounds in other solvents. Unfortunately, most of these have to be excluded from Table 2, because the

TABLE 2.

Comparison of rate constants of rearrangements of various hydrazo-compounds (RNH·NHR') by the two-proton (k_3 in sec.⁻¹ mol.⁻² l.²) and one-proton (k_2 in sec.⁻¹ mol.⁻¹ l.) mechanisms.

R	R'	μ *	k_3	k_2	Ref.†
At 0°, in "60%" aqueous dioxan containing perchloric acid					
Phenyl	Phenyl	0.05	0.0017	—	15
<i>o</i> -Tolyl	<i>o</i> -Tolyl	0.1	0.0085	0.00021	VII
<i>p</i> -Tolyl	<i>p</i> -Tolyl	0.05	1.40	—	15
2-Naphthyl	Phenyl	0.1	0.0050	0.00050	VI
1-Naphthyl	Phenyl	0.1	0.13	0.020	V
2-Naphthyl	2-Naphthyl	0.06	—	0.46	III
1-Naphthyl	2-Naphthyl	0.05	—	1.0	II ‡
1-Naphthyl	1-Naphthyl	0.05	—	1.8	I
At 0°, in "95%" aqueous ethanol containing hydrochloric acid					
Phenyl	Phenyl	0.1	0.0024	—	12a
<i>o</i> -Tolyl	<i>o</i> -Tolyl	0.05	0.0075	0.00025	12b §
<i>m</i> -Tolyl	<i>m</i> -Tolyl	0.05	0.015	—	12c ¶
<i>p</i> -Tolyl	<i>p</i> -Tolyl	0.03	1.24	—	12d

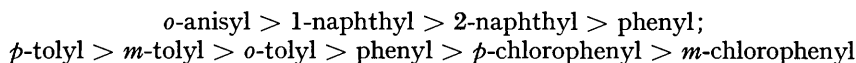
* Concentration of total uni-univalent electrolyte. † The Roman figures refer to Parts of this series.¹ The other numerical references are to the footnotes in this Paper. ‡ Rate adjusted for medium, using data in Parts III and V.¹ § Rate constants recalculated by means of equation I (p. 2868). ¶ Rate extrapolated for temperature.

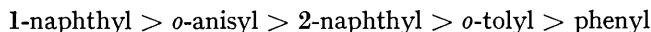
applicability of the formula used to calculate them was not established. After Hammond and Shine had rediscovered the quadratic dependence on acid of the rearrangement of hydrazobenzene in aqueous ethanol, it was widely assumed that this exclusive rate-law would apply to all hydrazo-compounds and all solvents; thus the practice grew up of recording even a single measurement of rate as a k_3 value, without controlling the actual acid-dependence of the rearrangement measured. These figures are all unreliable on the evidence given, and some of them are certainly incorrect. The main exception to these statements is contained in the careful work of Carlin and his associates on the rearrangement of hydrazobenzene and a series of its dimethyl derivatives in "95%" aqueous ethanol.¹² These figures do allow rates to be compared in relation to substrate structure, and they are accordingly given in the lower part of Table 2. Again, the salt conditions are not completely uniform, but are sufficiently nearly so to permit the intended comparison of substrates.

A series of rate constants for the rearrangement of hydrazo-compounds by the one-proton mechanism (k_2 of equation 1, p. 2868) in "60%" aqueous dioxan is given in the fifth column of Table 2. Once again, the salt conditions vary a little, but not enough to upset the comparisons to be made. We have no further comparative series, but we have a single value, from the work of Carlin and Odioso,^{12b} applying to solvent "95%" aqueous ethanol, as shown in the lower part of Table 2.

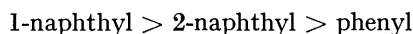
The data of Table 2, supplemented by some other measurements, not yet complete enough to publish, involving anisyl and chlorophenyl groups, allow the aryl groups of hydrazo-compounds to be arranged in the following series, according to their effect in accelerating rearrangement:

Two-proton Mechanism:



One-proton Mechanism:

Using the rate-data, as well as certain qualitative observations in Parts XII—XIV,¹ we can write the following short sequence of groups in order of their effect on the non-catalytic rate of rearrangement.

No-proton Mechanism:

These series strongly suggest that electron-release by the aryl groups, such as would promote electron-transfer from one nitrogen atom to the other in the hydrazo-compound, is the dominant constitutional factor controlling rates of hydrazo-rearrangements. This is consistent with the polar-transition-state theory. There are special features of the series, particularly the position of the *p*-tolyl group as an outstandingly accelerating influence in the two-proton mechanism, for which an explanation will be suggested in Section 15, after some details of the polar-transition-state theory have been filled in.

(6) *Salt Effects on Rate of Rearrangement.*—Since 1950, most workers on the kinetics of acid-catalysed benzidine rearrangements have noticed that these reactions are strongly accelerated by added neutral salts.^{11,12,14} These observations have applied until recently to the two-proton mechanism of rearrangement. However, the work recorded in the previous Parts of this series disclosed that comparably large accelerative effects of salts arise also in the one-proton mechanism of rearrangement (Parts I, III, V, VI, and VII¹). The one-proton mechanism does seem to be slightly less salt-sensitive than the two-proton mechanism (Part V), but both are highly sensitive.

If the marked accelerating effects of salts had applied only to the two-proton mechanism, one might possibly have tried to interpret it, although its large magnitude would have created a difficulty, on the basis that extra polarity arises in the transition state from the concentration there of charges which in the initial state were spread between two separate, solvated, hydrogen ions. However, the appearance of comparable accelerating effects of salts in the one-proton mechanism, in which there is only one ionic charge in the transition state, and one in the initial state, shows that such an explanation would have been inadequate. It follows that some more fundamental cause must be sought for the undoubtedly large increment of polarity which the reacting system acquires on passing from its initial state to its transition state. New charges must have been created in this process, as, indeed, is required by the polar-transition-state theory of the rearrangement. The slight increase in salt-sensitivity in the two-proton relative to the one-proton mechanism may be due to the collecting together in the transition state of the former previously separated ionic charges.

We may note how this large positive salt effect, common to the two-proton and one-proton mechanisms, bears on other theories of the benzidine rearrangement. As to the π -complex theory, the observed salt effect has nothing to say. For although the π -complex intermediates assumed in the theory have been described, the transition states of their formation and decomposition have not, and hence such assumptions as are needed to fit the kinetic facts could still be built into the theory.

The large positive salt effect is incompatible with the caged-dissociation theory. As we have seen, this theory in its standard form does not accommodate the one-proton mechanism. In its application to the two-proton mechanism, it predicts only a small positive salt effect, contrary to the observations. For the transition state consists of the two separating radical-ions, and hence the main effect on the ionic atmosphere arises only from the collection of previously more widely scattered charges into neighbouring ionic entities. A similar situation arises when we try to modify the caged-dissociation theory for application to the one-proton mechanism; the assumption now is that the addition of

the single proton is succeeded by a heterolysis to give a cation and a molecule, contained in the same solvent-cage. In the production of the transition state of this process, an ionic charge, originally on a solvated hydrogen ion, is transferred first to one nitrogen atom of the hydrazo-compound, and then, as the heterolysis progresses, to the other one, though this second transference will be only partial in the transition state itself. Thus the theory predicts a small negative salt effect, again contrary to the observations.

(7) *Solvent Effects on Rearrangement Rate.*—The effect of solvent polarity on the rate of a benzidine rearrangement by the two-proton mechanism was studied systematically by Croce and Gettler.¹³ The example was the rearrangement of hydrazobenzene in mixtures of ethanol and water in various proportions. The water-contents of the mixtures were all much more than enough to allow full solvation by water of the ions of the catalysing acid. Within the investigated range of conditions, an increase of water-content accelerated rearrangement. As noted in Part III,¹ the observed form of the dependence of rate on the dielectric constant of the medium was qualitatively inconsistent with electrostatic theory at any known level of refinement at which its application to mixed and to pure solvents would be identical; however, the dependence could be understood if we might assume that the electrostatic fields around the transition state are strong enough to separate the components of the medium, the more polar water concentrating towards the transition-state charges.

Complementing Croce and Gettler's work on the two-proton mechanism, we have examined solvent effects on rates of rearrangement by the one-proton mechanism. The examples were the acid-catalysed rearrangements of 1,1'- and 2,2'-hydrazonaphthalene in aqueous organic solvent mixtures (Parts I and III.¹) Two oppositely tending effects were observed.

When the water-contents were under a certain low threshold, rearrangement was accelerated by further reduction in the water-content. This can be understood on the basis that at low enough water-contents, the catalysing hydrogen ion will be solvated only partly by water, and also partly by the organic component of the medium. The composition of the solvation shell, and hence the activity of the hydrogen ion, will then be sensitive functions of the water-content, the activity rising sharply as the water-content is reduced. Therefore the pre-equilibrium protonation of the substrate, and in consequence the rate of its rearrangement, will rise sharply as the water-content is reduced.

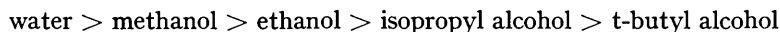
A different situation revealed itself in media containing enough water to ensure that solvation of the catalysing hydrogen ions would be practically wholly by water. The rearrangement rate was now examined over two types of solvent variation, one that in a series of different organic solvents, running from strongly to weakly polar, all mixed with a common proportion (5 vol. %) of water, and the other that of mixtures of the common organic solvent dioxan with different proportions (5—40 vol. %) of water. The results were mutually consistent. In the first series, the rate rose with the polarity of the organic component of the medium, and in the second it rose with the water-content of the aqueous dioxan. The form of the rate variation in the latter series was very similar to that which Croce and Gettler had previously found in a similar study of the two-proton mechanism in the example of hydrazobenzene.¹³ As we have seen, this form of variation required the assumption that water is selectively withdrawn from the mixed solvent by electric charges developed in the transition state of rearrangement. A semi-quantitative comparison of the sensitivity of rate by the two mechanisms to medium composition could be made, and it emerged that the one- and two-proton mechanisms were comparably sensitive. We therefore conclude that, for the one-proton mechanism, as for the two-proton mechanism, over the relevant range of water-content, the main cause of the variation of rate with medium composition is the variable degree to which water is selectively withdrawn from the mixed medium by the electric charges developed during the formation of the transition state of rearrangement.

We have to conclude that the one- and two-proton mechanisms have comparable

potentials in this respect, just as, according to a conclusion drawn in Section 6, they have comparable potentials for the development of ionic atmospheres, which particularly stabilise the transition state, in the presence of neutral salts. Thus the common conclusion to be derived from the study of kinetic salt effects and polar solvent effects on the two mechanisms is that the dominating polarity developed in both types of acid-catalysed transition state depends essentially on charges created by the rearrangements, and not on charges taken over from the respective initial states as added protons.

This is consistent with the polar-transition-state theory of the rearrangements. For reasons given in Section 6, it is agnostic with respect to the π -complex theory, and is inconsistent with all forms of the caged-dissociation theory.

The no-proton rearrangements, that is, the non-catalytic ("thermal") rearrangements, have been investigated with respect to solvent effects on rate by Shine in the example of 2,2'-hydrazonaphthalene,^{20a,b} and by ourselves in that of 1,1'-hydrazonaphthalene (Part XII¹), with mutually consistent results. The data, illustrating solvent effects on rate, which are available for either or both of these examples, may be summarised as follows. (i) Rates of rearrangement in hydroxylic solvents as a class are substantially greater than in non-hydroxylic solvents, polar or non-polar. (ii) Among hydroxylic solvents, high rates follow polarity, as illustrated in the solvent series:



(iii) Among non-hydroxylic solvents, rates again follow polarity, as shown by the solvent series:



From these results, the conclusion follows that although the initial state is electrically neutral and only weakly polar, and although the transition state is also electrically neutral as a whole, nevertheless, in polar solvents at least, strong charge-separations are developed in the transition state as a necessity of the rearrangement. This is consistent with the idea that the transition state in non-catalytic rearrangement develops largely electrostatic bonds as pictured by the polar-transition-state theory for the two acid-catalysed forms of rearrangement. In other words, the kinetic effect of polar solvents in non-catalytic rearrangement suggests that the no-proton mechanism, and the one-proton and two-proton mechanisms, despite the differences of net charge in their transition states, develop strongly polar bonds in an analogous way, thereby achieving large increments of polarity in their transition states.

The π -complex theory is inapplicable to non-catalytic rearrangement. The caged-dissociation theory is applicable, if it be assumed that the neutral hydrazobenzene molecule first dissociates into a pair of caged neutral radicals. But there would then be a negligibly small effect of polar solvents on reaction rate, contrary to the observations.

It should be emphasised that these conclusions concerning non-catalytic rearrangement apply only to this reaction in polar solvents. On the evidence presented, nothing can be said of the non-catalytic mechanism in non-polar solvents.

(8) *Acid Dependence of Rearrangement Rate at Higher Acidities.*—The matter of mechanism to which the experiments summarised in this section and the next one were addressed was that of whether, in acid-catalysed benzidine rearrangements, the addition of the proton, or of each proton when two are involved, is an equilibrium process, and in any single molecular system is complete before the transition state of rearrangement is reached, or is a kinetically controlled process, and is only in progress in each system when this is passing through its transition state. If all catalytic proton transfers are equilibria, then the rate should follow a scale of acidity designed to measure equilibrium proton-transferring power; the scale we have used is Hammett's h_0 scale. If the proton transfers are kinetically controlled, then the rate should follow more closely a measure of acidity more relevant to encounter-probabilities, the hydrogen-ion concentration $[H^+]$. The method has diagnostic

value only at acidities above those at which h_0 and $[H^+]$, when defined to be the same at low acidities, begin strongly to differ. Because there is a practical upper limit to the rates that we could measure, this restriction to somewhat high acidities, and hence to high rates, has limited the direct evidence obtained by this method to the two-proton mechanism. For, whilst substrates showing stable two-proton kinetics can be examined in the diagnostic acidity range, substrates which show one-proton kinetics up to the highest acidities examined would react much too rapidly for kinetic measurements by our methods at acidities of significance in the present connexion. Again, all the known substrates which show transitional kinetics are reacting essentially by the two-proton mechanism in the diagnostic range of acidities. However, despite this restriction of direct evidence, we lose very little in conclusions; for the results have so turned out that a common conclusion embraces both the protons involved in the two-proton mechanism, and hence, by a very strong implication, the single proton added in the one-proton mechanism.

In our solvent, "60%" aqueous dioxan, the Hammett function, $H_0 = -\log h_0$, of perchloric acid is known above $[H^+] = 0.1N$; and it diverges strongly from $-\log [H^+]$, so becoming diagnostic, when $[H^+]$ is above $0.25N$. In four cases, those noted in Table 3,

TABLE 3.

Acidity ranges and results of comparisons of functions of specific rate k_1 with functions of $[H^+]$ and h_0 in "60%" aqueous dioxan containing perchloric acid.

Example no.	(1)	(2)	(3)	(4)
R,R' in RNH·NHR'	Ph ₂	(<i>o</i> -Tolyl) ₂	2-Naphthyl, Ph	1-Naphthyl, Ph
log k_1 vs. log $[H^+]$ {	Range $[H^+]$...	0.05—0.25		
	Relation	Linear		
" " {	Slope	2.00		
	Range $[H^+]$...	0.25—1.00	0.016—0.50	0.02—0.30 *
" " {	Relation	Curved	Curved	Curved
	Range $[H^+]$...		0.016—0.30	
$k_1/[H^+]$ vs. $[H^+]$ {	Relation		Linear	
	Data given.....		k_2, k_3	
" " {	Range $[H^+]$...	0.25—1.00	0.30—0.50	0.02—0.30 *
	Relation	Curved	Curved	Linear
" " {	Data given.....	—	—	k_2, k_3
	Range $[H^+]$...			0.10—0.25
log k_1 vs. $-H_0$ {	Relation			Curved
	Range $[H^+]$...	0.10—1.00	0.10—0.50	0.10—0.60
" " {	Relation	Linear	Linear	Linear
	Slope	2.1	2.2	2.13
References †	15, VIII	VII	VI	V

* Solvent "70%" aqueous dioxan. † The figure 15 refers to reference 15, and the Roman figures to Parts of this series.¹

a comparison of $\log k_1$, the logarithm of the specific rate of rearrangement at a fixed acidity, has been made first with $\log [H^+]$ from low acidities upwards, and then with $-H_0$ from $[H^+] = 0.1N$ upwards, as far into the diagnostic range above $0.25N$ as kinetic measurements can be made. In the example (1), of hydrazobenzene, the two-proton mechanism operates throughout the whole range of the kinetic observations, and the plot of $\log k_1$ against $\log [H^+]$ is linear with a slope of 2.00 from low acidities to $[H^+] = 0.25N$, above which $\log k_1$ diverges, just as $-H_0$ would diverge, from continued linearity with $\log [H^+]$. On the other hand, the plot of $\log k_1$ against $-H_0$ is linear with a slope of 2.1 from $[H^+] = 0.1N$ upwards, and, in particular, well into the diagnostic range, from $[H^+] = 0.25N$ to $1.0N$ the limit of the measurements. The wide divergence of $\log k_1$ from linearity with $\log [H^+]$ above $[H^+] = 0.25N$, a divergence which testified to the significance of the restoration of linearity when the acidity function is changed from $\log [H^+]$ to $-H_0$, has been graphically illustrated.¹⁵

The examples (2)—(4) in Table 3 involve substrates which show mixed one-proton and two-proton kinetics at acidities below the diagnostic range. When such transitional kinetics are in operation, no linear relation is found between $\log k_1$ and $\log [H^+]$, but a

linear relation should be, and is, found between $k_1/[H^+]$ and $[H^+]$, provided that the acidities remain below the threshold above which $[H^+]$ diverges from h_0 . Those linear relations give the second- and third-order rate-constants, k_2 and k_3 , of the partial rates under the one- and two-proton mechanisms, respectively. In examples (2) and (3), the two-proton mechanism is in practically full charge at acidities around and above the diagnostic threshold; and from below to well above that threshold, the plots of $\log k_1$ against $-H_0$ are linear, with slopes of 2.2 and 2.13, respectively. In example (4), the two-proton mechanism is in less than complete control at the threshold of the diagnostic acidities, and hence the linearity of $\log k_1$ with $-H_0$ in the two-proton mechanism can be tested only over a somewhat short range of acidities; however, the data do point to a linear relation, with a slope of 2.1.

There can be no doubt that the Hammett slopes of 2.1—2.2, shown in the penultimate line of Table 3, represent an idealised slope of 2, identical with the slope, found in example (1) to be 2.00, for the same two-proton mechanism, in conditions such that $[H^+]$ values are low enough to be identical with h_0 values. There are three reasons why these observed Hammett slopes might be a little different from their ideal value: (a) there was a temperature difference between the determinations of H_0 at 20° and of k_1 at 0°; (b) the comparisons of $\log k_1$ should have been, had H_1 been known, with $H_0 + H_+$, rather than with $2H_0$, and it is an assumption, only indirectly supported, that H_0 and H^+ can be taken as parallel functions; and (c) although the indicator-base, *p*-nitroaniline, providing the H_0 scale, was probably the most suitable that could have been chosen (some further confirmation of this has since appeared²¹), no indicator-base is suited quite perfectly to parallel the equilibria of kinetic interest.

The fact that we must use Hammett acidities, in order to secure linear relations, which remain linear at the higher acidities, means that, of the added protons involved in the two-proton mechanism, which is the operative mechanism in all our examples, *both* are added completely in any individual molecular system before its transition state of rearrangement is attained.¹⁵ In short, these experiments are consistent with specific hydrogen-ion catalysis in both of the hydrogen ions, with no typical incursion of general-acid catalysis, not even with respect to the proton which is added second, and hence against the repulsion of the proton added first. All this is consistent with what we should intuitively expect. For, any general-acid catalysis in the two-proton mechanism would imply that the rate of all the processes needed to complete rearrangement after uptake of the second proton is greater than the rate of back-transfer of a proton to the basic solvent from the extremely strongly acidic, doubly charged cation. As this back-transfer must be almost non-activated, with a specific rate therefore approaching 10^{13} sec.⁻¹, a higher rate for the remaining processes of the rearrangement is difficult to contemplate.

It cannot be doubted that the single proton involved in the one-proton mechanism, which is not *directly* examined by this particular method, is added in pre-equilibrium, just as completely in any individual molecular system as is the second proton in the two-proton mechanism. The alternative would be to envisage one and the same substrate (for the same substrate may employ the two-proton and one-proton mechanisms) which (a) would require two protons to be completely added before achieving activation, and yet (b) would not require one proton to be more than partly added before achieving activation. From this *reductio ad absurdum*, we infer that the one-proton mechanism, equally with the two-proton mechanism, is a matter of specific hydrogen-ion catalysis. We support this conclusion by *direct* observation on the one-proton mechanism by another method, as outlined in Section 9. We shall compare all these conclusions with the requirements of theories of the benzidine rearrangement, after the evidence obtained by the second method has been summarised.

(9) *Kinetic Effect of Solvent Deuterium on Acid-catalysed Rearrangements.*—These experiments were likewise addressed to the question of the stage of entry of the catalytic

²¹ Jørgenson and Hartter, *J. Amer. Chem. Soc.*, 1963, **85**, 878.

proton or protons. If a proton is only in the process of being transferred in the transition state, its binding there being weaker than in the initial state, second differences of zero-point energy will produce a slower reaction, when the proton is replaced by a deuterium. For reaction thus catalysed by a single hydrogen ion, the factor of retardation by deuterium is often about 7 ± 2 . On the other hand, if a catalytic proton is transferred in pre-equilibrium, a deuterium will be more extensively transferred than a proton, because D_3O^+ is a stronger acid in D_2O than H_3O^+ is in H_2O ; hence the deuterium-catalysed reaction will go faster. For most reactions acid-catalysed in this form by a single hydrogen ion, the factor of acceleration by deuterium is usually 2.0 ± 0.3 .

We have carried out comparative rate measurements on the same substrate in a mixture of 60 vol. of dioxan with 40 vol. of water, and in a mixture of 60 vol. of dioxan with 40 vol. of deuterium oxide, the acid, salt, and temperature conditions being the same. We have examined four substrates in this way, which between them embrace the one-proton and two-proton mechanisms of rearrangement. In all cases, rearrangement went faster in the deuterium solvent. This is a first indication that the transfers of protons, even of the second one when there are two, are all pre-equilibria. The important figures are in Table 4.

TABLE 4.

Effect on rates of hydrazo-rearrangements, catalysed by perchloric acid at 0° , of changing the solvent from 60 vol. of dioxan with 40 vol. of water to the dioxan mixed with 40 vol. of deuterium oxide.

Substrate	$[H^+]$ or $[D^+]$	Order in $H^+ (= x)$	k_D/k_H ($= y$)	$f_m = * f(x, y)$	Ref.: Part no.
1-C ₁₀ H ₇ ·NH·NH·C ₁₀ H ₇ -1	0.010	1.0	2.3	2.3	I
2-C ₁₀ H ₇ ·NH·NH·Ph	{ 0.020 0.31	{ 1.15 1.75	{ 2.6 3.8	{ 2.2 2.1	{ VI VI
<i>o</i> -MeC ₆ H ₄ ·NH·NH·C ₆ H ₄ Me- <i>o</i>	{ 0.010 0.29	{ 1.25 1.9	{ 2.1 3.5	{ 1.8 1.9	{ VII VII
Ph·NH·NH·Ph	0.19	2.0	4.8	2.2	I

* The positive root of $(x - 1)f_m^2 + (2 - x)f_m - y = 0$.

The example of rearrangement involving only one-proton kinetics was that of 1,1'-hydrazonaphthalene. The factor of acceleration, k_D/k_H , by solvent deuterium found in this example, was 2.3. This is in the normal range of such factors for reactions acid-catalysed by the transfer in pre-equilibrium of a single proton.

The substrate illustrating only two-proton kinetics was hydrazobenzene. The factor of acceleration by solvent deuterium observed in that case was 4.8, the largest such factor yet recorded for any reaction. However, two protons are involved, and the mean factor, f_m , per transferred proton will be the square-root of 4.8, namely, 2.2, again a normal value for one proton transferred in pre-equilibrium. Moreover, the unknown, individual, single-proton factors, which by multiplication build up the observed factor, 4.8, must obviously each lie fairly close to their geometric mean, 2.2. Therefore, *each* of the successively transferred protons, even the second one, must be transferred in pre-equilibrium.

The remaining examples in Table 4 relate to substrates which show transitional kinetics of rearrangement. In this area, one can change the effective order in acid, without having simultaneously to change the substrate, by an alteration of the acidity, and hence of the proportions in which the one-proton and two-proton mechanisms contribute to the observed rate; and then one can change the substrate as an independent act. The data show that the order in acid is the important factor determining the acceleration by solvent deuterium, though the constitution of the substrate plays a minor role. For any substrate and any acidity, for which the order in acid and the factor of acceleration by solvent deuterium are determined, we can assign a mean factor, f_m , of acceleration to each of the involved proton-transfers, that is, a mean factor per proton, which, if assigned to the single proton transfer of the one-proton mechanism, and to each proton transfer in the two-proton mechanism, would combine (the law of combination is given below the Table) to

produce the factor, k_D/k_H , of acceleration observed for the overall reaction. All these mean factors per proton, f_m , are in the range 2.0 ± 0.2 and hence in the range of normal values for accelerations by solvent deuterium of reactions acid-catalysed by one proton transferred in pre-equilibrium. A further conclusion follows from the close grouping of the values, notwithstanding that each substrate has been examined in two sets of conditions, one giving predominance to the one-proton and the other to the two-proton mechanism. This conclusion is that no one of the three individual factors of acceleration, associated with the separate proton transfers, can differ very much from their functional average f_m . It follows from the whole set of results in Table 4 that all the transferred protons, the single one in the one-proton mechanism, and each of the two successively transferred in the two-proton mechanism, notably the second one, must be transferred in pre-equilibria.

These conclusions, and the identical conclusions of Section 8, though derived by different methods, agree with the assumptions of the polar-transition-state theory of benzidine rearrangements.^{3b} They disagree with the assumptions of the π -complex theory, which envisages an intuitively improbable, general-acid catalysis with respect to the second catalytic proton, when this is kinetically significant,^{5e, f, g} and does not accommodate the one-proton mechanism among the naphthyl hydrazo-compounds. They agree with the caged-dissociation theory of the two-proton mechanism,⁸ but that theory does not accommodate the one-proton mechanism at all, and could not contemplate the kind of situation that shows itself in transitional kinetics.

(10) *Effects of Aromatic Deuterium on the Acid-catalysed Reaction.*—Two aromatic hydrogen atoms must be lost in order to establish one biaryl bond. We have replaced these hydrogen atoms by deuterium atoms in different pairs of positions concerned in biaryl linking, and have examined the effect of so doing on the rate of rearrangement, and on the proportions in which the products are formed. The examples used were the acid rearrangements of hydrazobenzene (Part X¹) and of 1,1'-hydrazonaphthalene (Part IX¹) in "60%" aqueous dioxan.

The reaction of hydrazobenzene illustrates the two-proton mechanism of rearrangement. The competing modes of biaryl linking are 4,4' to form benzidine, and 2,4' to give diphenylene. The proportions are, respectively, 73 and 27, and are independent of acidity. 2,2'-Biaryl linking does not arise. One of the deuterated forms of hydrazobenzene examined contained deuterium in all four *ortho*-positions, and indeed, because the compound was then easier to prepare, in all four *meta*-positions as well. We knew that we could neglect the possibility of an appreciable secondary isotope effect of *meta*-deuterium on either mode of biaryl linking; this was confirmed in the event, because even a primary isotope effect of deuterium in the positions of the linkings could not be detected. The other deuterated hydrazobenzene contained deuterium in both *para*-positions.

The acid rearrangement of 1,1'-hydrazonaphthalene was our example of the one-proton mechanism. Its modes of biaryl linking are 4,4' to give naphthidine, and 2,2' to give two products, *viz.*, the 1,1'-diamine, known as dinaphthylene, and the dibenzocarbazole, which is its imine. 2,4'-Biaryl linking does not arise. The two 2,2'-linked products are independent end-points of the rearrangement, even though the diamine can be converted into its imine, *i.e.*, the dibenzocarbazole, in conditions different from those of the rearrangement. The proportions of the 4,4'-biaryl-linked diamine, the 2,2'-linked diamine, and the 2,2'-biaryl-linked imine are 63, 18, and 18, respectively, and are independent of acidity in the range of known kinetics. The two deuterium derivatives examined each contained two deuterium atoms; in one derivative they were in the 2,2'-positions, and in the other in the 4,4'-positions.

The data obtained in these experiments on hydrazobenzene and 1,1'-hydrazonaphthalene, each studied comparatively in three forms, the all-protium, the *ortho*-deuterated, and the *para*-deuterated forms, are summarised in Table 5. Some of the deuterated substrates contained less than the theoretical proportions of deuterium; the proportions found in them are noted in the Table. It was, however, shown (Part XI¹) that, when less

TABLE 5.

Comparisons of rates and proportions of products of rearrangement among isotopically modified forms of hydrazobenzene under second-order, and of 1,1'-hydrazonaphthalene under first-order, acid catalysis.

Hydrazobenzene	D, % of theor.	$k_2 = *$ $k_1/[H^+]^2$	4,4'-Linked diamine (%)	2,4'-Linked diamine (%)
All-H	—	0.00280	71.8	27.2
2,6,2',6'-} D_8	80	0.00287	71.4	27.9
3,5,3',5'-}				
4,4'- D_2	100	0.00285	72.8	26.2

1,1'-Hydrazonaphthalene	D, % of theor.	$k_2 = \dagger$ $k_1/[H^+]$	4,4'-Linked diamine	2,2'-Linked diamine (%)	imine (%)
All-H	—	1.65	63.6	17.0	16.7
2,2'- D_2	85	1.64	63.1	6.5	29.5
4,4'- D_2	90	1.63	62.3	18.1	18.5

* In "90%" EtOH with HCl at 0°; k_2 in sec.⁻¹ mole⁻². † In "60%" dioxan with HClO₄ at 0°; k_2 in sec.⁻¹ mole⁻¹ l.

deuterium was found than is required to fill the intended positions, all that was present was in those positions.

The mean rates quoted in Table 5 are believed to be good to about 1%. It is clear that neither deuteration in the *ortho*-positions, nor in the *para*-positions, affects the rate of rearrangement of either hydrazobenzene, or 1,1'-hydrazonaphthalene. The product determinations were independent, and hence do not add up accurately to 100%; but the mean figures quoted are believed to be reliable to about 2–3% of their individual values. These figures show that neither deuteration in the *ortho*-positions, nor in the *para*-positions, affects either the ratio of the 4,4'-linked to the 2,4'-linked product of rearrangement of hydrazobenzene, or the ratio of the 4,4'-linked product to the total of 2,2'-linked products of rearrangement of 1,1'-hydrazonaphthalene. On the other hand, 2,2'-deuteration, but not 4,4'-deuteration, markedly changes the internal ratio of the two 2,2'-linked products of rearrangement of 1,1'-hydrazonaphthalene, *viz.*, the diamine and the dibenzocarbazole.

These results lead to conclusions about the sequence of three events, the two aromatic-proton detachments involved in the establishment of the biaryl bond, and, where it occurs, the loss of ammonia leading to the imine (the dibenzocarbazole). The uniform lack of any isotope effect on overall rates of rearrangement shows that all these events must take place after the main transition states of rearrangement have been passed. This applies alike to the doubly protonated transition state of rearrangement of hydrazobenzene and the singly protonated one of that of 1,1'-hydrazonaphthalene.

As to the order of these events among themselves, the positive isotope effect of the 2,2'-deuteration of 1,1'-hydrazonaphthalene on the proportions in which the 2,2'-linked diamine and its imine arise, points to conclusions, with which the various null isotope effects on product proportions are fully consistent. We shall first show that the loss of ammonia could not be concurrent with the detachment of the first of the two transferred aromatic hydrogen atoms.

The ratio, r , of rates in the parallel branch-paths which end, the one in the diamine, and the other by ammonia loss in the imine:

$$r = (\text{rate in branch to amine})/(\text{rate in branch to imine}),$$

is experimentally observed. Averaged over the available data (Part IX¹) for the all-protium form of 1,1'-hydrazonaphthalene and for its 4,4'-dideuterated modification, the ratio r was 1.00 ± 0.01 . (The round figure is fortuitous.) For the 2,2'-dideuterated form, however, the value was 0.220 ± 0.007 . The factor F , by which the relative rate of formation of the diamine becomes reduced in the last-mentioned substrate, is thus

4.5 ± 0.2 . So large a factor could not arise if ammonia loss competed with the detachment of the first of the transferred aromatic protons, for the following reason. Provisionally, suppose that these two processes, were in competition. In the 2,2'-dideuterated substrate used, 85% of the 2- and 2'-positions were occupied by deuterium atoms in statistical distribution. Hence the material contained 72% of the 2,2'-dideutero-compound, 26% of the 2-monodeutero-derivative, and 2% of the all-protium parent. If, in the hope of achieving consistency with observation, we try to deduce as large a factor F as possible, we have to assume a large kinetic isotope effect for first-hydrogen transfer, that is, a large ratio:

$$d_1 = (\text{rate of 1st-H loss})/(\text{rate of 1st-D loss}).$$

Now the effect of assuming a large d_1 in raising the resulting F is self-limiting, because a large d_1 will ensure that most of the 26% of monodeuterated compound will lose 2-protium, rather than 2-deuterium, and will do so at the relatively high rate now being assumed for proton loss. By making the extreme assumption that the isotope ratio d_1 approaches infinity, we can calculate an upper limit to the factor F by which the ratio r could be found to be reduced in the 2,2'-deuterated substrate, if the ammonia loss were indeed concurrent with detachment of the first aromatic proton. This calculated value is 3.5, which is, of course, an upper limit higher than any conceivably realisable value. But it is lower than the actually observed value, 4.5 ± 0.2 , by much more than the experimental error.

No such inevitable difficulty arises under the assumption that the elimination of ammonia is a concurrent alternative to the detachment of the second aromatic hydrogen atom. However, the isotope effect on second-hydrogen loss, as expressed in the ratio

$$d_2 = (\text{rate of 2nd-H loss})/(\text{rate of 2nd-D loss}),$$

which we must assume in order to account for the factor F by which the ratio r of rates in the competing branch-paths is observed to be reduced in the 2,2'-dideuterated substrate, depends on what is assumed for the isotope effect, expressed by d_1 , on the antecedent first-hydrogen loss. Some correlated values of d_1 and d_2 , which in combination would lead to the observed value of F , are as follows:

d_1	10	7	5	3	2	1
d_2	5.4	5.7	6.0	6.6	7.9	12.1

These are possible values for hydrogen-isotope effects, and a number of them would be very normal values. Because the first-hydrogen transfer must occur at a higher part of the reaction co-ordinate, *i.e.*, nearer the main transition state, than the second, we should expect the first transfer to have the smaller local energy barrier, and accordingly the smaller isotope effect. Thus a pair of d -values within the range of the last four pairs listed above seems to be indicated.

Our picture is thus of two transfers of aromatic hydrogen atoms which are not concerted processes, because a competing reaction can be found which deflects material from one, obviously the second, but not from the first. In rearrangement proceeding through a singly protonated transition state, the transfer of the second aromatic hydrogen atom at least must be considerably activated. The transfer of the first is likely to be less activated. The transfers attending rearrangement through a doubly protonated transition state may well be less activated than the respectively corresponding transfers associated with the singly protonated transition state.

A further deduction can be drawn from the null isotope effect of 2,2'- and 4,4'-deuteration on the ratio in which 2,4'- and 4,4'-biaryl linking, and even 2,2'- and 4,4'-biaryl linking, takes place. It follows from this that the bifurcation in the path of rearrangement, which predetermines the eventual position of biaryl linking, must occur, not only before the aromatic hydrogen losses, but also at a point on the reaction co-ordinate sufficiently more energised to secure that an isotope restriction in one of the bifurcated

routes cannot divert material into the other route. This means that, if there is a single transition state in control of the overall rate of rearrangement, the bifurcation which determines the orientation of biaryl linking must at latest constitute the first feature on the reaction co-ordinate after the transition state. Of course, according to the evidence presented here, the bifurcation might occur within the transition state, or even before it, in the latter case creating two transition states which would operate in parallel.

(11) *Effects of Aromatic Deuterium on the Uncatalysed Reaction.*—In non-catalytic rearrangement, the kinetic effect of aromatic deuterium is different from that characteristic of the acid-catalysed reaction, sufficiently so to indicate a different placing on the reaction co-ordinate of the aromatic proton losses relatively to the main, rate-controlling, transition state. This matter has been examined (Part XII¹) in the example of the rearrangement of 1,1'-hydrazonaphthalene in the neutral polar solvents ethanol, acetonitrile, and acetone. The measurements were of the effect of deuterium, in the aromatic positions which rearrangement will connect with a biaryl bond, on the total rate of rearrangement. In contrast to the acid-catalysed rearrangement, there was a positive isotope effect on rate. In ethanol, it was somewhat small, corresponding to a reduction by a factor of 2—3 in the rate of establishment of the biaryl linking in a position which requires displacement of two aromatic deuterium atoms. In acetonitrile, and in acetone, the effects were larger and nearly equal; they corresponded to reductions by factors estimated to be of the order of 6 in the rate of establishment of a biaryl bond between deuterated aromatic positions. This is quite a normal value for a primary isotope effect in a reaction in which hydrogen is undergoing transfer as an important part of the transition-state process.

The immediate inference from these results is that, in the non-catalytic rearrangement, the loss of at least one of the two protons, that have to be transferred from the aromatic ring, has been pushed back to an earlier point on the reaction co-ordinate than it occupied in the acid-catalysed rearrangement, back, indeed, into the region of the main, rate-controlling, transition state. We shall rationalise this conclusion below on the basis that the loss of the first, not of both, of the two lost aromatic protons would be expected to be pushed back towards the transition state in the non-catalytic mechanism. In Section 14, we shall deduce from evidence of another kind that, whilst in the non-catalytic mechanism the loss of the first aromatic proton is indeed comprised within the transition state, the loss of the second lies definitely beyond it, and is one of the last events of the mechanism.

If the one-proton and no-proton mechanisms are analogously heterolytic according to the pattern of the polar-transition-state theory, there will be a difference of charge distribution in the transition states, which will profoundly affect the ease of transfer of the first of the two lost aromatic protons, but will not much affect the loss of the second. For the strong electrostatic element, which that theory assumes in the binding within the transition state between its two aromatic moieties, will be of the cation-dipole type in the transition state of the one-proton mechanism, but of the cation-anion type in that of the no-proton mechanism. The electrons that will form the new biaryl bond must come from the less positive aromatic ring, that is, from the dipolar ring in the one-proton, and from the quasi-anionic ring in the no-proton, transition state; and either electron-donating ring will then receive a substitute pair of electrons from its hydrogen atom, as the latter becomes expelled as a proton. This hydrogen, always the one from the less positive of the two aromatic moieties, will be the first of the two aromatic hydrogen atoms to be expelled. The second will be subsequently lost from the pseudo-cationic moiety. But that portion of the structure is the same in both transition states. Hence the isotopic difference between the mechanisms will be felt essentially only in the loss of the first aromatic hydrogen atom.

As compared to the transfer of this particular proton from the dipolar aromatic portion of the one-proton transition state, we should look for a considerably facilitated transfer from the ring in the quasi-anionic portion of the no-proton transition state. The reason is an expected predisposition of this proton to move to the neighbouring main seat of

negative charge in the quasi-anionic aromatic moiety, *viz.*, its amidic nitrogen atom. (The corresponding nitrogen atom of the one-proton transition state bears a positive charge, inasmuch as it is the positive end of the dipole characterising the moiety.) If, in the no-proton mechanism, the recovery of electrons from hydrogen by the aromatic ring were on this account made so much easier that it became concurrent with the supply of electrons from the ring to form the new biaryl bond, we should observe a kinetic isotope effect when the transferred proton was replaced by a deuterium.

The tendency, in the negative moiety of the no-proton transition state, of the "ortho" aromatic proton to move over to the neighbouring amidic nitrogen atom is expected to be reduced by hydrogen-bonding solvation of the latter; for such solvation constitutes a competitive method of neutralising the amidic charge. We can thus understand that in a hydroxylic solvent, such as ethanol, the transfer of the aromatic proton would attain less importance in the transition state than it would in non-hydroxylic solvents, such as acetonitrile and acetone; and accordingly that the deuterium-isotope effect on rate of rearrangement would be smaller in ethanol than in acetonitrile or acetone. These were indeed the experimental findings (Part XII¹).

We do not compare the one-proton and no-proton mechanisms on the basis of either the π -complex or the caged-dissociation theories of the benzidine rearrangement, because each of these theories is inapplicable to at least one of the mechanisms.

(12) *Products of Acid-catalysed Rearrangement.*—Hammick and Munro observed^{4b} that *para*-semidines, which appear among the products of aqueous acidic benzidine rearrangements when heavy-metal ions are present during reaction, are not produced when heavy-metal ions are absent. Heavy-metal ions were often present in the earlier work on benzidine rearrangements, because a convenient and commonly used experimental method of producing such rearrangements was to reduce an aromatic azo-compound by a metal dissolving in an acid, and, without isolating the hydrazo-compound formed, to allow it to rearrange in the acid solution in which it was formed. There are other situations in which *para*-semidines may be formed, but all in some way involve what may be regarded as an inessential complication in the conditions. Thus the conclusion seems justified that *para*-semidines, when they appear, arise from mechanisms more complex than any with which we wish now to be concerned. This conclusion legitimises the simplification, which we shall adopt, of excluding *para*-semidines from the following considerations concerning the isomers reported to have been found in the products of the acid-catalysed rearrangements of hydrazo-compounds.

One matter of products seems to be somewhat separate from the ensuing general survey, and to be connected in its general indications with a conclusion derived from the work outlined in Section 10. This conclusion, which followed from the absence of an isotope effect of aromatic hydrogen on the rates of acid-catalysed rearrangements, was that the bond, which is to become a biaryl bond, is established as a bond before either of the aromatic protons, which will have to be displaced, are actually lost. The related matter of rearrangement products concerns the loss of 4-carboxylic and 4-sulphonic acid substituents in hydrazobenzene, during rearrangement to benzidine; the substituents are eliminated very readily, and benzidine is formed practically completely.²² It would be difficult to picture this loss of substituents except from a cyclohexadiene ring, which, by absorbing the electron-pair which held the substituent, recovers aromatic character. This implies a sequence of events analogous to that assumed for some irreversible electrophilic aromatic substitutions, such as nitration, namely, that the bond to the entering substituent is established first to form a cyclohexadiene derivative, and that the displaced group is expelled in a subsequent fast step, and accordingly, if it is hydrogen, without an isotope effect on substitution rate.

It has been reported²² that 4-chloro-, 4-bromo-, and 4-acetoxy-substituents, though

²² Jacobson, *Annalen*, 1922, 428, 76.

retained in the main products of the rearrangements in which they participate, may undergo some elimination in the formation of benzidine and *para*-semidines as minor products. However, the reducing experimental conditions employed would allow these eliminations to be reductive, the substituent leaving in possession of its bond electrons as halide or acetate ion. This is in contrast to the eliminations of carboxylic and sulphonic acid substituents considered above, which are oxidative in the sense that the group leaves as carbonate or sulphate, *i.e.*, without its bond electrons. Reductive elimination may be connected with the unknown mechanism of *para*-semidine formation.

We now turn to the orienting effect of substituents on the aromatic positions in which biaryl and *ortho*-semidine linkings occur in the rearrangements of hydrazo-compounds. This has been considered by Dewar,⁵⁹ who has offered "a few simple rules" on the subject as follows.

- (1) Overall preference: 4,4'- > 2,4'- > 2,N'-linking.
- (2) In 2,4'-linking, 4' is *para* to the more basic nitrogen.
- (3) In 2,N'-linking, N' is the less basic nitrogen.

The relative basicities of the nitrogen atoms of the hydrazo-compound are taken qualitatively to parallel those of the primary amines obtainable from it by reduction (the "fission amines").

These rules have been quoted, but their representation of the observations is not satisfactory. The first of the two inequalities of rule (1) does express a broad trend among the more simply substituted *NN'*-diphenylhydrazines. However, exceptions arise even in this area; and when one benzo-substituent is present as in *N*-1-naphthyl-*N'*-phenyl-, or two as in *NN'*-di-1-naphthyl-hydrazine, even the broad trend is different, as Dewar recognises, *e.g.*, 4,4'- ~ 2,2'-linking in these examples.¹ The second inequality in rule (1), which, if true, would be important when a 4-substituent blocks 4,4'-linking, represents a preference in these circumstances for a 2,4'-linked diphenylene, rather than a 2,N'-linked semidine; however, this does not correspond to the observations. As we shall note below, which one of these two modes of linking is favoured depends on the 4-substituent; the known examples are comparatively divided between the two possibilities.

As for rule (2), we are at a complete loss as to its observational basis. It purports to describe, in case a diphenylene is formed, which of the two alternative modes of diphenylene linking, 2,4' or 4,2', will preferentially occur. However, rule (2) can have no meaning unless (a) both 4- and 4'-positions are free, (b) at least one 2- and at least one 2'-position is free, and (c) the two benzene rings are non-equivalent. Among more than 100 examples of hydrazo-rearrangements, known to us through the literature or by observation, there is not one which fulfils these conditions and has been observed to give any diphenylene at all.

Dewar's rule (3), which should apply when blocking 4-substituents promote *ortho*-semidine formation, claims to prescribe which nitrogen atom is then involved in the semidine linking. However, once again, the rule does not follow the observations. As we shall note below, semidine linking may take either of the two possible directions, 2,N' or N,2', depending on the nature of the 4-substituent; the known examples are comparably divided between these alternatives.

Dewar derives his rules from his π -complex theory, and then states, without supporting detail, that the rules summarise the observations.⁵⁹ The latter pronouncement is clearly incorrect.

The broad trends regarding biaryl linking in 2- and 4-positions correspond to relative quinonoid stabilities in the benzo- and naphtho-series. In the former, the *para*-quinonoid bond-arrangement is the more stable. The accepted reasons are quantal, and can be traced back to the resonance principle, or the variation principle, or, of course, the uncertainty principle. Thus the trends can be understood as meaning simply that bond distributions

in the transition states of the rearrangements are highly quinonoid in character.^{3a} However, some of the most striking facts are not thus simply interpreted. In the acid rearrangement of hydrazobenzene in "60%" aqueous dioxan, 73% of 4,4'-linking occurs, and 27% of 2,4'-, but no 2,2'- *at all*. This is clearly not just a matter of relative 2- and 4-reactivities in either ring, and it cannot be referred back to independent tendencies in each ring to use *ortho*- or *para*-quinonoid transient bond-arrangements. The true explanation must bring in some mutual relation between the two rings. In the acid rearrangement of 1,1'-hydrazonaphthalene, and even in that of *N*-1-naphthyl-*N'*-phenylhydrazine, comparable amounts of 4,4'- and 2,2'-linking occur, but no 2,4'- *at all*. The same conclusions apply. In order to interpret such facts, which point to orientation by ring-interaction, we must consider the mechanism in more detail, as we shall do in Section 15.

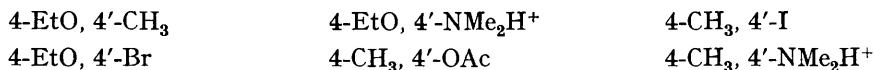
Carlin and his co-workers have shown²³ that, on substitution of hydrazobenzene in *meta*-positions by four like substituents, 2,2'-biaryl linking in rearrangement becomes appreciable. It is associated, if the common *meta*-substituent is fluorine, with an increase in 4,4'- at the expense of 2,4'-linking, and, if it is chlorine, bromine, or methyl, with an increase in 2,4'- at the expense of 4,4'-linking. No kinetic study of these reactions has yet been recorded, so that we have not this important control upon interpretation; but the product compositions may possibly point to a mixture of polar and steric effects.

The regularities of orientation which appear to us to be disclosed by the observations at present available are as follows. As a preliminary classification we shall group the data under five heads.

First, we summarise the effect of a single 4-substituent, in promoting one or other of the alternatives of 2,4'-diphenylene formation and *ortho*-semidine formation. When 4-R has a strongly dominating or exclusive polar effect of electron-release, an *ortho*-semidine is essentially the only rearrangement product. The available illustrations cover 4-R = OEt, OMe, CH₃; and there are upwards of a dozen examples, and no exceptions. When 4-R is either weakly polar or electron-attracting only, the other alternative path, that leading to a 2,4'-diphenylene, is the one chosen by the reaction. The illustrations cover 4-R = H, OAc, NMe₂H⁺ (if we suppose that an introduced NMe₂ group is effectively protonated under the conditions); there are about ten examples, and no exceptions. The halogens exert not only strong electromeric electron-release (which is orientationally, though not kinetically, dominating in electrophilic aromatic substitutions) but also strong inductive electron-attraction (kinetically dominating in electrophilic aromatic substitution). When 4-R = Cl, Br, I, both *ortho*-semidines and 2,4'-diphenylenes are formed, the latter preponderating.

Secondly, we examine the effect of a single 4-substituent, 4-R, such as promotes *ortho*-semidine formation, in determining whether the semidine linking will be 2,*N'*- or *N*,2'-. The observations show that, when 4-R = OEt, OMe, CH₃, Cl, Br, I, the semidine link is exclusively 2,*N'*-. On comparing these results with Dewar's rule (3), we see that OEt, OMe, and CH₃ follow the rule, whereas Cl, Br, and I act in opposition to it.

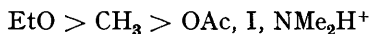
Thirdly, we summarise findings on the orienting effect of the simultaneous presence of two substituents in 4- and 4'-positions. Whatever they are, provided that they are not eliminated, these substituents must jointly promote *ortho*-semidine formation. If they are non-equivalent, the question arises as to which of the alternative modes of *ortho*-semidine formation will be preferred. The observations show that, when unlike substituents are present in the following pairs



the link established in rearrangement is practically exclusively 2,*N'*. Thus, a 4-sub-

²³ (a) Carlin and Forshey, *J. Amer. Chem. Soc.*, 1950, **72**, 793; (b) Carlin and Heininger, *ibid.*, 1955, **77**, 2272.

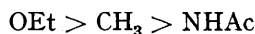
stituent directs *ortho*-semidine linking towards the 2-position of its own aromatic ring in the following order of orienting strengths



In so far as this series is ordered, the order is one of decreasing electron-release.

Fourthly, we consider orientation by a single 2-substituent, and also by a pair of substituents in 2- and 2'-positions. The observations show that a single 2-substituent of a type that can exert strong electron-release orients biaryl linking practically exclusively towards the 4-position of its own aromatic ring; and furthermore, that, when two such substituents are present in 2- and 2'-positions, each of them acts in that way. The available illustrations cover 2-R = OEt, OMe, CH₃, Cl; there are about twenty examples, and no exceptions. When the 4- and 4'-positions are both free, a 4,4'-benzidine is the sole rearrangement product. When the 4-position is free but the 4'-position is blocked, a rearrangement, oriented by a 2-substituent as specified, should lead to a 4,2'-diphenylene, and the observations show that a 4,2'-diphenylene is indeed the sole rearrangement product (apart from any *para*-semidine that may be formed in the presence of heavy-metal ions). There are five recorded examples, and no exceptions.

Fifthly, and finally, we summarise the evidence as to the relative orienting strengths of substituents in 2-positions. The comparison between substituents cannot now be made quite as direct as it was in the corresponding study of orientation by substituents present in 4-positions, because substituents, which, when separately present in a 2-position, would orient biaryl linking to the 4-position, when present together in the 2- and 2'-positions, can lead only to a 4,4'-linked benzidine, a product which gives no information as to the relative orienting strengths of the substituents. However, a 2-substituent and a 4'-substituent, if present together, would be in orientational competition, although orientation from the group in the 2-position is towards the 4-position, and orientation from the 4'-position is directed to the 2'-position. But the products are different; orientation by a 2-substituent towards position-4 leads to a 4,2'-diphenylene, whilst orientation from a 4'-substituent towards position-2' leads to an *N*,2'-semidine. Comparisons among orienting groups in these conditions are possible, and the known examples, which are mutually consistent, give the following order of control



At each inequality here, we have a change in the direction of orientation, 2 \longrightarrow 4, as we may symbolise it, going over into 4 \longrightarrow 2, as well as the change in the orienting group. However, the general result is so similar to that given by our previous analysis of orientation by substituents in 4- and 4'-positions, where the direction is always 4 \longrightarrow 2, as to suggest that similar factors apply in both directions, and that this ordered series, like the previous one, indicates electron-release as the essential basis of orientation.

These are the five collations of the available observations concerning effects of substituents on the orientation of rearrangement. The sources of most of the observations can be found in Jacobson's summarising Paper.²² We do not think that they have been accurately and rationally analysed before. To be fair to the record does not mean that one is satisfied with the observations. One cannot rest satisfied with the data until at least a representative sample of all observations made before 1950 on products of benzidine rearrangements has been quantitatively revised in conditions of measured kinetics, as is a main programme in these laboratories.

Our analysis was in five parts, because we were following the pattern set by the available observations. It remains to combine the five conclusions in a single statement of the orientational principles which the data appear to disclose. This is as follows:

A 4-substituent, if strongly electron-donating, leads to 2,*N'*-linking, if not, to 2,4'-linking, and if both strongly donating and attracting (halogens), to both modes of

linking; an electron-donating substituent, if at 4, orients linking towards 2, and if at 2, towards 4, with a strength paralleling that of its electron-donation.

It stands out clearly from these conclusions that the orientation of biaryl and semidine linking is essentially a polar phenomenon. This would be demanded by the polar-transition-state theory. It is inconsistent with the caged-dissociation theory. The particular form that polar orientation takes is inconsistent, as we have seen, with the π -complex theory. It will be discussed more constructively in Section 15, in relation to the particular features there treated of the polar-transition-state mechanism.

Bearing in mind that electron-releasing groups in 2- and 4-positions accelerate rearrangement (Section 5), the above statement of orientational principles might be taken as describing activated *meta*-orientation, a phenomenon forbidden in the general theory of electrophilic aromatic substitution. However, such a reading of the orientation-rate pattern of the benzidine rearrangement would be very superficial, inasmuch as it treats the two aromatic moieties of the rearranging molecule as independent, whereas they must be interacting. In particular, the electron-releasing substituent helps to put negative charges into the other aromatic ring, not into its own ring (cf. Section 15).

(13) *Dependence of Products on Kinetic Order in Acid.*—The revision on quantitative lines, and under conditions of known kinetics, of earlier work on the compositions of products of benzidine rearrangements has been begun. Carlin and his collaborators¹² have quantitatively analysed the products formed from hydrazobenzene, and from its 3,3'- and 4,4'-dimethyl derivatives in rearrangements quadratic in acid, and those from the 2,2'-dimethyl derivative in a rearrangement of kinetic order 1.6 in acid. When it became known that this fractional order signalised concurrent but independent mechanisms, a strong reason was provided why all subsequent product determinations should refer to kinetically controlled conditions. This then became the new mode of product study. The most interesting cases are those in which we can change the kinetics without changing the substrate, and so record the effect purely of a change of mechanism on products. The available data in this field are almost entirely contained within the papers of the present series, and are collected in Table 6.

As indicated by the signs explained in footnotes *b* and *c* to Table 6, some product determinations are given which refer to acidities, and therefore to rearrangement rates, which are higher than could be studied kinetically by our techniques. However, the law under which kinetic order changes with acidity is so clear (Section 3) that we may count on its continuing operation at acidities above the verified range. This means that, if at lower but rising acidities we can directly observe the first part of a rise of order in acid from 1 towards 2, we may assume that the rise will continue towards the limit of 2 as the acidity is further increased. One does in fact find changes of product composition that are compatible with this assumption. In one case, that of 1,1'-hydrazonaphthalene, we cannot observe even the beginnings of a rise of order in acid above unity before the rate, rising with acidity, goes out of range of the kinetic observations; but if we make the reasonable assumption that, at acidities much higher than the highest that we can reach kinetically, a substantial increase in kinetic order will occur, then observed changes of product proportions at such higher acidities can be correlated with similar changes found in other examples, in which the evidence of a rising kinetic order is more direct.

Table 6 discloses two effects of kinetic form, and thus of mechanism, on product composition. The first is seen in the data on *N*-1-naphthyl-*N'*-phenylhydrazine; it is that a change from the one-proton to the two-proton mechanism increases the proportion of 4,4'- at the expense of 2,2'-biaryl linking. Though we have only one good example, we expect this effect to be general. We attribute it to an assumed electrostatic effect of the second proton in the transition state of the two-proton mechanism in lengthening *N*-*N'* and 2-2', relatively to 4-4', distances. It is consistent that, as comes out in the examples of 2,2'-dimethyl- and 2-methoxy-hydrazobenzene, included in Table 6, when the

TABLE 6.

Dependence of product compositions ^a on acidity ^b and kinetic order ^c in rearrangements in "60%" aqueous dioxan at 0°.

Substrate	[H ⁺] (M)	Order in acid	4,4'-Linked	2,4'-Linked	2,2'-Linked	Ref. ^d
2,2'-Dimethyl-hydrazobenzene	0.03	1.4	100	0	0	C, VII
	0.50	2.0	100	0	0	VII
2-Methoxy-hydrazobenzene	0.01	1.5	100	0	0	R
	0.30	2.0	100	0	0	R
<div style="display: flex; justify-content: space-around;"> 4,4'-Linked 2,2'-Linked </div>						
1,1'-Hydrazo-naphthalene	Up to 0.03	1.0	63	19	18	I, IX
	<2.5	?	—	—	10	I
	<4.5	?	—	—	3.5	I
N-1-Naphthyl-N'-phenylhydrazine	0.08	1.4	45	43	12	V
	<1.0	?	60	33	6.5	V
	<2.0	?	65	31	4	V
<div style="display: flex; justify-content: space-around;"> 3-Linked 1,1'-Linked </div>						
2,2'-Hydrazo-naphthalene	Up to 0.1	1.0—1.2	0	94	5.7	III
	<0.6	?	—	—	4.6	III
	<2.4	?	—	—	2.0	III
	<4.5	?	—	—	ca. 0.0	III
<div style="display: flex; justify-content: space-around;"> 1,4'-Linked 1,2'-Linked </div>						
N-2-Naphthyl-N'-phenylhydrazine	0.05	1.3	0	99	0.5	VI ^e
	0.50	1.85	0	99	ca. 0.0	VI ^e

^a In cols. 4—6, product compositions are in moles % of total rearrangement products. ^b The sign < means that reaction must have taken place at acidities lower than that of the figure given, because the time of reaction was comparable to, or less than, the time taken to mix in the acid. ^c The sign ? means that, in the circumstances noted under *b*, although the kinetic order is not observed, it must be rising towards 2 as the acidity is increased, and, where above 1 at kinetic acidities, must be close to 2 at the highest nominal acidities. ^d The numerals refer to Parts of this series,¹ C means observations by Carlin and Odioso^{12b} under not quite the same conditions, and R means observations by Jyotibhusan Roy to be recorded in a forthcoming Part of this series. ^e In this example, the kinetics are at 0°, and the products are those of reaction at 20° under otherwise identical conditions.

one-proton mechanism leads only to 4,4'-biaryl linking, the two-proton mechanism does not change this result.

The second effect of kinetic form, and hence of mechanism, on product composition is even sharper, and appears in four of the examples in Table 6. This is that, when the one-proton mechanism is either observationally known or reasonably concluded to be undergoing replacement by the two-proton mechanism, then the formation of derivatives of carbazole (called "imine" in Table 6) is largely, if not completely, suppressed. We think that the two-proton mechanism cannot in principle produce a carbazole, because, in order to secure the substitution which eliminates ammonia, one nitrogen atom has to be in basic and the other in cationic form, and the second proton in the two-proton mechanism destroys the required basic centre.

(14) *Products of Non-catalytic Rearrangements.*—Data are available for the rearrangements of 1,1'- and 2,2'-hydrazonaphthalene, N-1- and N-2-naphthyl-N'-phenylhydrazine, and hydrazobenzene. They have been studied with respect to products in the solvents ethanol, acetonitrile, acetone, and benzene, at 80—110°, and in the solid state at 110—130° (Parts XII—XIV¹). The first two compounds have been studied with respect to kinetics (Shine; ^{20a,b} and Part XII¹). In ethanol, acetonitrile, and acetone, the first-order rate-law is obeyed. In benzene, a more complicated kinetic situation is revealed. In the reactions in benzene, and in the solid state, tars and *para*-semidines may appear among the products. Krolik and Lukashevich have shown²⁴ that *para*-semidines are

²⁴ Krolik and Lukashevich, *Doklady Akad. Nauk S.S.S.R.*, 1960, **135**, 1139.

formed by hydrazo-rearrangements in the presence of acid, provided that insufficient solvent is taken to dissolve the hydrazo-compound, so that a solid phase co-exists with the solution. We infer that the decompositions in benzene and in the solid substances, without acid, involve more-complex mechanisms than any with which we are now concerned. We shall therefore confine further discussion of the compositions of the products formed in non-catalytic conditions to the apparently simpler reactions which occur in the polar solvents ethanol, acetonitrile, and acetone.

Table 7 collects results in this field in summarised form from the Papers cited. An important further contribution has recently been made by Lukashevich and Krolik.²⁵ They have examined the compositions of the products of the uncatalysed rearrangement

TABLE 7.

Abundances of products of uncatalysed decompositions of hydrazo-compounds in polar solvents at 80—100°. (The italicised figures are due to Lukashevich and Krolik.²⁵)

Solvents	MeOH	MeOH + MeONa	EtOH	EtOH + EtONa	MeCN	Acetone
<i>1,1'-Hydrazonaphthalene</i>						
4,4'-Biaryl-linked	25	25	20, 16	24	4	0
2,2'-Biaryl-linked	31	25	34	34	+++	+++
The carbazole	25	0	30, 25	0	10	10
Disproportionation	24	25	+++	22	+++	+++
<i>1,2'-Hydrazonaphthalene</i>						
2,1'-Biaryl-linked	87	—	—	89	76	—
The carbazole	53	—	—	0	43	—
Others recovered	2	—	—	1	14	—
<i>2,2'-Hydrazonaphthalene</i>						
1,1'-Biaryl-linked	—	—	99	90	97	93
The carbazole	—	—	19	0	21	22
Disproportionation	—	—	0	5	3	8
<i>N,1-Naphthyl-N'-phenylhydrazine</i>						
4,4'-Biaryl-linked	—	—	++	—	+++	++
2,2'-Biaryl-linked	—	—	+++	—	++	+++
The carbazole	—	—	+	—	+	+
Disproportionation	—	—	0	—	0	0
<i>N,2-Naphthyl-N'-phenylhydrazine</i>						
1,2'-Biaryl-linked	—	—	100	—	98	97
The carbazole	—	—	7	—	9	5
Disproportionation	—	—	0	—	3	4
<i>Hydrazobenzene</i>						
4,4'-Biaryl-linked	—	—	+	—	+	+
2,4'-Biaryl-linked	—	—	+++	—	+++	++
2,N'-Semidine	—	—	0	—	+	+++
Disproportionation	—	—	+	—	++	++

of 1,1'-hydrazonaphthalene in 22 media, and of those of its 1,2'- and 2,2'-isomers in smaller numbers of media. This work has been criticised in Part XII,¹ but only with respect to the rearrangements of the 1,1'-compound in the aprotic media, and many acceptable results remain, the most significant of which are included in Table 7.*

The figures in Table 7 are percentages in which the hydrazo-compound is decomposed to form the several products, that is, they are percentages of total rearrangement plus any accompanying disproportion to azo-compound and fission amines. The statements of abundance of "ortho-linked," that is, 2,2'-, 1,1'-, and 2,1'-biaryl-linked, products always include both the primary diamine and its imine, the carbazole; but the carbazole item is also given separately (and so the two figures must not be added), because the production of this substance has to be separately discussed. Some of the analyses are partly qualitative,

* The reservations we have as to their quantitative accuracy are not important here.

²⁵ Lukashevich and Krolik, *Doklady Akad. Nauk S.S.S.R.*, 1962, **147**, 1090.

mainly because unsurmounted difficulties in the standardisation of diazotisation conditions prevented colour intensities derived from fully separated materials from being quantitatively translated into percentage amounts of the latter. Therefore, use is again made of the order-of-magnitude indications, + + +, + +, and +, for primary, secondary, and trace products, respectively, according to the rough scale explained in Part XII.¹

The most general feature of these results is their overall similarity with those obtained for the acid-catalytic rearrangements of the same substrates. For 1,1'-hydrazonaphthalene, the products of rearrangements in the neutral solvents are just the three formed in acid media. For the 1,2'-isomer, the main and secondary products are the same. For the 2,2'-isomer, the rearrangement products in the neutral reactions are just the two of the acid reaction in similarly unbalanced proportions. For *N*-1-naphthyl-*N'*-phenylhydrazine, the same two major products and the same secondary product are formed in neutral conditions as in acid. For the *N*-2-naphthyl isomer, the same major and minor products, and even the same two trace products (cf. Part XIII¹), constitute the whole of the rearranged material in the two sets of conditions. These five comparisons are of rearrangements by the no-proton mechanism with rearrangements by the one-proton-mechanism. The comparison concerned with hydrazobenzene will be between the no-proton and two-proton mechanisms; thus some greater dissimilarity might be expected. The non-catalytic rearrangement of hydrazobenzene gives, not only benzidine and diphenylene, the sole products of the acid-catalysed rearrangement of this substance, but also another rearrangement product, *viz.*, *ortho*-semidine.

These general similarities predispose one to think that a broad analogy exists between the mechanism of these non-catalytic rearrangements in polar solvents and the mechanisms of the acid-catalytic reactions. Our view is that they are all essentially heterolytic. We shall show in Section 15 that this assumption leads to the expectation of a similarity of the products of the no-proton mechanism to those of the one-proton mechanism. Shine's view²⁰ that neutral hydroxylic solvents act through their hydroxylic hydrogen atoms, more or less analogously to acids, fits in well with the general conclusion.

From this point on, our interest centres mainly on the differences between the compositions of the products of the non-catalytic and acid-catalytic rearrangements, especially in those differences which appear to be systematic. One such difference comes out most clearly in the example of 1,1'-hydrazonaphthalene. It is that, when acid conditions are replaced by neutral, there is a shift of product composition away from predominantly 4,4'- and towards predominantly 2,2'-biaryl linking. The indication that the shift is systematic is that it strengthens markedly as the solvent becomes less polar (and kinetically slower) along the series ethanol, acetonitrile, acetone. It seems possible to understand this on the basis of the polar-transition-state picture, according to which the strong electrostatic element in the binding in the transition state between the two aromatic moieties is of the ion-dipole type in the one-proton mechanism, but of the ion-counterion type in the no-proton mechanism; wherefore, in the non-catalytic mechanism, we might expect a closer binding, stronger N-N attraction during the formation of the transition state, and hence a smaller shift from the initial to the final position of binding, than in the catalytic mechanism. This special feature of the non-catalytic mechanism should appear more markedly in generally less polar solvents, which, because of their incapacity to solvate the charges strongly, would favour tighter transition-state structures. The effect should be least apparent in the hydroxylic solvents, which, if only by hydrogen bonding, will largely neutralise negative charges, as on the amidic nitrogen atom in the negative moiety of the non-catalytic transition state.

A second matter for comparison between the acid-catalytic and non-catalytic mechanisms concerns the loss of ammonia during rearrangement to give part of the "*ortho*-linked" product as an imine, *i.e.*, a carbazole derivative. We have already found evidence (Section 13) that the two-proton mechanism cannot produce carbazoles. The one-proton mechanism certainly does produce them. So does the no-proton mechanism in general.

However, as Lukashevich and Krolik discovered,²⁵ it does not do so when an alcoholic solvent is used which is made strongly basic with the corresponding alkoxide ion. They showed that what, in the absence of the alkoxide, would have been carbazole, appears in its presence as an extra quantity of the "ortho" diamine. The short summary is that carbazole formation requires an optimum degree of protonation, and is suppressed by too little or too much. This is a strong argument for the view that the bond-changes, alike in non-catalytic and catalytic rearrangement, are essentially heterolytic. For the elimination of ammonia then requires one nitrogen atom to be in basic, and the other in cationic, form; too much protonation will destroy the basic centre, and too little the cationic. The alkoxide ions evidently deprotonate the reacting system.

It is significant that the suitable degree of protonation for carbazole formation spreads over two mechanisms, and is not confined to one. The one-proton and no-proton mechanisms, which both yield carbazoles, differ in the degree of protonation in their main, *i.e.*, rate-controlling, transition states. The requirement of protonation at the moment of the ammonia elimination must, we assume, be quite sharp. Therefore, one mechanism or the other must undergo an adjustment of protonation between passage of the system through the main transition state and its arrival at that bifurcation of path at which ammonia loss leading to carbazole competes with an aromatic proton loss which results in an "ortho" diamine.* In order to achieve, within the framework of an intramolecular mechanism, the degree of protonation that is expected to optimise carbazole formation in the no-proton mechanism, one has to assume proton donation, whether by transfer or by hydrogen bonding, from the solvent to the reacting system, so building up there, after the main transition state has been passed, a charge situation analogous to that in the one-proton mechanism. This is the charge situation, which is required to take care of the closing steps of rearrangement, in particular, the ammonia elimination, with which an aromatic proton loss is in competition. We assume that our solvents, ethanol, acetonitrile, and acetone, can all act in this way—unless what they do is undone by an added strong base, such as a lyate ion.

In Section II, we noticed isotopic evidence that, in the no-proton mechanism, the transference of at least one of the two aromatic hydrogen atoms that have to be displaced in order to accommodate a biaryl bond is contained within the main transition state of the mechanism. The isotopic observations themselves left it open as to whether the conclusion to which they pointed applied only to the first of the two transferred aromatic protons, or to both of them. However, a theoretical interpretation on the basis of the polar-transition-state theory indicated that the conclusion from the isotopic evidence should apply only to the first of the protons transferred. We now have evidence of another kind to the effect that one of the two transfers of aromatic hydrogen, that which is competitive with ammonia loss, occurs after the transition state has been passed, indeed, sufficiently long after to allow adjustments of protonation in between. All this, when put together, constitutes a complete case for the view that, in the no-proton mechanism, as in the one-proton, and almost certainly the two-proton mechanism (cf. Section 9), the transfers of the two aromatic hydrogen atoms constitute separate and successive mechanistic steps. Our isotopic evidence bears on the first step, and the evidence concerning products bears on the second. It is satisfactory that the only theoretical interpretation which we have been able to devise, that given by the polar-transition-state theory, demands just such a separation between the processes of proton transfer.

The remaining matter of apparently systematic differences of products between the acid-catalytic and non-catalytic mechanisms relates to hydrazobenzene. We are now comparing the two-proton mechanism with the no-proton mechanism. In the two-proton mechanism, 4,4'-linked benzidine is the chief product, and 2,4'-linked diphenylene is the

* A similar phenomenon might be involved in Hammond and Clovis's observation¹⁷ of a dependence of product composition on acidity without change of kinetic form in the acid rearrangement of 3,3'-diaminohydrazobenzene.

only other rearrangement product. As we pursue the no-proton mechanism through our solvents in order of decreasing polarity, ethanol, acetonitrile, acetone, the preponderating 4,4'-biaryl-linked benzidine of the two-proton mechanism becomes progressively replaced in the no-proton mechanism, first, by 2,4'-linked diphenylene, and then by the eventually preponderating 2,*N'*-linked semidine. We shall refer again to this result in Section 15.

(15) *Stereochemical Interpretations of Products and Rates.*—Up to now, we have discussed observations bearing on the mechanism of the benzidine rearrangement in relation to three theories of mechanism, *viz.*, the polar-transition-state, the π -complex, and the caged-dissociation theories. But the case that has accumulated against the latter two theories seems now sufficient to exclude them. The π -complex theory is out of accord, for example, with the one-proton mechanism in the naphthalene series, with the independent concurrence of the one- and two-proton mechanisms, with specific hydrogen-ion catalysis in the two-proton mechanism, and with the observed dependence of products on structure. The caged-dissociation theory is incompatible, for example, with the one-proton mechanism, with the no-proton mechanism in polar solvents, with salt and solvent effects on rate, and with the dependence of products on structure. On the other hand, the polar-transition-state theory has met all the demands made on it so far. We shall therefore simplify treatment of the subject of this Section by discussing it from the standpoint of polar transition-state theory alone, apart from an occasional passing reference for comparison to one of the other theories.

We have reserved for discussion here matters apparently dependent on the stereochemistry of the transition state of rearrangement. As to this, the polar-transition-state theory offers wide accommodation, but also imposes some restrictions, which have orientational importance in particular cases. The assumed leading heterolysis of the N-N bond will make it largely electrostatic, abnormally long, and abnormally weakly directed, so allowing similarly constituted replacing bonds to be formed, which will go into well-directed, normal-length, covalencies, as finally they shorten. It has been noted that largely electrostatic bonds can maintain the integrity of the rearranging structure at much greater extensions, such as 5—7 Å, than can homopolar bonds,^{3b,c} and also that the weakly directed nature of the polar bonds is a major factor permitting easy shape changes.^{4a,3c} These are the factors of accommodation. The main factor of restriction is that transition-state charges are often concentrated on particular positions, which largely determine the configuration of minimum energy. In special cases, steric hindrance may constitute a second factor of restriction, though we have as yet no completely clear evidence on the matter.

Our first problem is that presented by the acid-catalysed rearrangement of hydrazobenzene; it gives 4,4'- and 2,4'-biaryl-linked products, in a 3 : 1 ratio in aqueous acetone, but no 2,2'-linked product at all. On following through the polar-transition-state mechanism in detail,^{3c} we find that, after double protonation followed by extensive N-N heterolysis, a transition state will be formed which contains an aromatic moiety with nearly two units of cationic charge; and that this structure is linked, largely electrostatically, to a second aromatic moiety, which overall is nearly neutral. We have to consider the charge distribution in these two parts of this transition state. The two approximate units of positive charge in the quasi-cationic system are not freely distributable; one is securely fixed on the ammonium nitrogen atom, and, because of this, the other, to minimise energy, is located almost wholly in the *para*-position [see (Ia)]. The bond-arrangement is thus quinonoid in an essentially static way, and the conjugation is more formal than functional in the sense of contributing to electron-delocalisation. A different situation prevails in the quasi-neutral aromatic moiety, which, because electron-delocalisation counterbalances electrostatic neutralisation, will be a dipole, like an aniline molecule, with the nitrogen as its positive end. In the ring, as is well understood for aniline, the distribution of negative charge is biased by electron-delocalisation towards *para*-, and by the electrostatic attraction of unlike charges towards *ortho*-positions, with the result that comparable negative

charges appear in all three positions [see (Ia)]. From these charge distributions alone it follows that the transition state can, in this approximation, form its new bonds only in the 4,4'- and 2,4'-positions, and not in the 2,2'-position. These considerations prescribe the stereochemistry of the transition state [see (Ib)]. For, the positive *para*-charge in the one

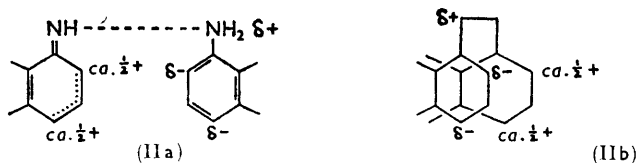


ring will be attracted towards the centroid of the negative charges in the other ring, and it is assumed that the easy flexibility of the C-N-N-C chain will allow the required relative longitudinal displacement of ring centres. The relative displacement will increase, as the electrostatic forces are strengthened, when the medium is made less polar; and, consistently, the proportion of 2,4'-linked diphenylene is, indeed, increased by such changes of medium.⁸

This description of the benzidine rearrangement has much in common with the mechanism established by Adams and his co-workers for the anodic oxidation of *NN*-dimethylaniline to *NNN*'*N'*-tetramethylbenzidine.⁹ The *NN*-dimethylaniline molecule might conceivably have passed into an intermediate by loss of only one electron to give a single-charged radical-cation; but in fact it lost two together, to give the doubly charged cation, which then attacked an unaltered *NN*-dimethylaniline molecule.

A contrasting problem is presented by the catalysed rearrangement of 1,1'-hydrazonaphthalene, which produces comparable amounts of 4,4'- and 2,2'-biaryl-linked products, but no 2,4'-linked product at all. Dewar tried to interpret this on the assumption that, in the π -complex of the rearrangement, the naphthalene residues are π -bonded together through both the component rings of each, and therefore cannot undergo the relative rotation needed to establish a 2,4'-bond.⁵⁹ If this were right, then, when we discard one of the four rings, and hence lose one of the two π -bond "anchors," as in *N*-1-naphthyl-*N'*-phenylhydrazine, rotation and its consequences should be restored. But they are not; the products from *N*-1-naphthyl-*N'*-phenylhydrazine are just like those from 1,1'-hydrazonaphthalene, and not at all like those from hydrazobenzene.

We assume^{3c} that, after the addition of a proton to 1,1'-hydrazonaphthalene, and after the N-N bond has become considerably heterolysed, a transition state is formed in which one of the two aromatic moieties bears nearly one unit of positive charge, whilst the other is nearly neutral but dipolar. The electron defect in the positive residue will reside almost entirely on carbon, as the element of smaller effective nuclear charge, where it will gain further stability by division, most of it in comparable shares between the 2- and 4-carbon atoms [see (IIa)]. The C=N bond does not appreciably contribute to the electron-delocalisation, and the unsubstituted ring contributes only in a minor way. The dipolar structure will resemble a 1-naphthylamine molecule, with the positive end of its dipole on the nitrogen

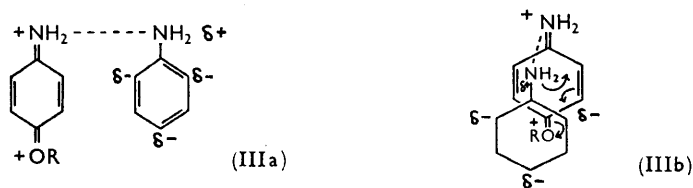


atom, and the negative end distributed in the aryl residue, again mainly and comparably between the 2- and 4-positions [see (IIa)]. Electron-delocalisation is general throughout

this system. The two aryl residues will therefore come together "congruently," that is, without longitudinal relative displacement [see (IIb)]. This rearrangement can therefore give only 4,4'- and 2,2'-biaryl-linked products, and cannot give a 2,4'-linked product.

A similar description applies to the rearrangement of *N*-1-naphthyl-*N'*-phenylhydrazine, except that here the direction of polarisation has first to be decided. This can scarcely be in doubt, inasmuch as the phenylamine nitrogen is expected to be considerably the more basic of the nitrogen atoms, and the naphthyl group much the better electron-donor of the two aryl groups. The quasi-cationic moiety of the transition state will therefore be like that derived from 1,1'-hydrazonaphthalene, and the quasi-molecular moiety like that from hydrazobenzene. These two residues also will converge without longitudinal relative displacement, and so, once again, the products will be 4,4'- and 2,2'-biaryl-linked, and not 2,4'-linked.

The first step in the interpretation of the rules, given in Section 12, for the orientation of rearrangement by substituents in the hydrazobenzene molecule is to interpret the effect of strongly electron-donating 4-substituents, such as methoxyl, in leading to a 2, *N'*-semidine. The direction of polarisation of the 4-methoxy-compound is unambiguous, and will make the anisylamine residue the quasi-cationic portion of the transition state. Its two approximate units of positive charge will be situated, the one, as in the example of hydrazobenzene, on the ammonium nitrogen atom, and the other remotely therefrom, but less now on *para*-carbon, and largely on the oxygen atom, which will accordingly assume oxonium character [see (IIIa)]. In the transition-state configuration, this quasi-cationic moiety, and the quasi-molecular, aniline-like, moiety, will suffer greater relative displace-



ment than was described for the rearrangement of hydrazobenzene, probably by a large fraction of a normal C-O bond-length [see (IIIb)]. In the quasi-cationic moiety, bond-forming electron-acceptance is possible only at the 2-position; and, because of the strong displacement, this position can be reached more easily by electrons from the nitrogen atom, than from any other atom, of the aniline-like moiety. Thus a 2, *N'*-semidine will result.

The 4-methyl substituent will act similarly, but by hyperconjugation, and hence more weakly. We can thus understand why, in competition, 4-methoxyl prevails over 4-methyl as an orienting influence. The 4-halogeno-substituents act more weakly still, presumably because their conjugation is considerably restricted by their electronegativity; and now only a part of the rearrangement product is the 2, *N'*-semidine. We can understand why, in all these examples, the *ortho*-semidine is the 2, *N'*-, and not the *N*, 2'-semidine.

When the 4-substituent is insufficiently electron-donating to produce these effects, the configuration of the transition state will revert towards that described for the rearrangement of hydrazobenzene. 4,4'-Biaryl linking being excluded by the substitution, the characteristic product will be a 2,4'-diphenylene. This forms part of the rearrangement product from any of the 4-halogenohydrazobenzenes, and all the product in some other examples, including hydrazobenzene itself, if in this case we discount the concurrent 4,4'-linking.

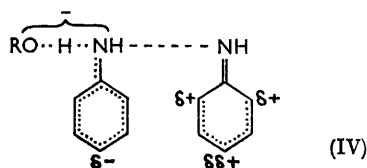
As to electron-donating 2-substituents at acidities leading to double protonation, we assume that, in the cationic moiety of the transition state, the second unit of charge, which electrostatic forces would place almost exclusively on the 4-carbon atom will be partly

transferred to the 2-substituent by its release of electrons, though the electron defect will still reside on the 4-carbon atom. We must distinguish between positive-charge distribution and electron-defect distribution, because all charges are stereochemically significant, whereas an electron defect useful for bonding is present in a carbonium centre, but not in an ammonium or oxonium centre. In the critical configuration, the charge transfer from the 4-carbon atom to the 2-substituent will lead to a reduced relative displacement of the rings, as compared to that described for the rearrangement of hydrazobenzene; hence the 4-carbon atom will combine with the 4'-carbon atom, if the latter is unsubstituted, to a greater extent than the approximate 75% characteristic of hydrazobenzene. If the 4'-carbon atom is substituted, the 4-carbon atom will combine with the 2'-carbon atom, provided that the 2-substituent is more strongly orienting than the 4'-substituent. Orienting strength is expected to follow electron-donating capacity, as, *e.g.*, in the descending order, alkoxy, alkyl, halogens. All these conclusions, indeed, all those of the last four paragraphs, agree with the recorded observations, as summarised in Section 12.

The transition state of non-catalytic rearrangement is expected to consist of a quasi-cationic portion, which is just like that described for one-proton catalysis, linked with a quasi-anionic, anilide-ion-like portion. In the latter, a large fraction of the negative charge will reside on the nitrogen atom, as the element of higher effective atomic number, though there will be a partial dispersal of charge by hydrogen-bonded solvation in protic solvents, and by electron-delocalisation over the aromatic ring. Most of that part of the overall negative charge, which, on account of electron-delocalisation, appears on aromatic carbon, will be carried remotely from the negative nitrogen atom. In a simple anilide residue it will be carried on the *para*-carbon atom, and in substituted anilide residues, partly there and partly on any electron-absorbing *para*-substituent that may be present, for instance, the unsubstituted ring of a 1-naphthylamide residue. The charge distribution over the transition state of non-catalytic rearrangement of 1,1'-hydrazonaphthalene will therefore be somewhat as in (II), apart from a changed sign of a fractional charge at one nitrogen atom; thus the rings will approach each other approximately congruently, and the transition state will lead to products essentially the same as those derived by the one-proton mechanism of acid catalysis. In the non-catalytic rearrangement of *N*-1-naphthyl-*N'*-phenylhydrazine, the leading heterolysis will carry electrons from the more basic towards the less basic nitrogen atom. The quasi-cationic portion of the transition state will have its positive charge distributed between the *ortho*- and *para*-positions of its phenyl group, whilst the quasi-anionic portion will be a 1-naphthylamide residue like that just described. Again, the residues will converge approximately congruently, so leading to products essentially the same as those of the one-proton rearrangement. The other non-catalytic rearrangements involving a naphthyl group can be similarly discussed and the conclusions are similar. The general correspondence of the products of the no-proton and one-proton mechanisms of rearrangement can thus be understood. Upon the general resemblance, certain differences are superimposed, solvent-dependent differences in the ratio of 2,2'- to 4,4'-biaryl linking, and base-dependent differences in the ratio of carbazole to diamine in the products of 2,2'-linking; these phenomena have been discussed in Section 14.

In the example of hydrazobenzene, no such close comparison of non-catalytic and catalytic transition states is possible, because the latter is a two-proton state; therefore we consider the non-catalytic rearrangement of hydrazobenzene separately. The quasi-cationic moiety of its transition state will have its positive charge distributed between *ortho*- and *para*-positions, with most on the *ortho*-positions, because the exocyclic double bond is essentially static, so that electron-delocalisation is concentrated on the pentadiene system, the ends of which will take most of the charge [see (IV)]. This is a further illustration of the need to distinguish formal from functional conjugation. The quasi-anionic moiety will have a large fraction of its negative charge on the nitrogen atom, or dispersed therefrom by hydrogen bonding with the solvent; and nearly all the rest of the charge

will be on the *para*-carbon atom [see (IV)]. This charge distribution over the two components of the transition state will favour 2,4'-biaryl linking. It will lead to ring convergence with a displacement, in which the negative *para*-carbon will overlie the centroid of positive charge in the other ring, so allowing easy 2,4'-linking. It is understandable that this orientational preference might be enhanced in a less polar solvent, in which more negative charge is transferred from the solvent to the substrate structure, and in which all



electrostatic attractions are increased. The observed results are that, in contrast to the predominating 4,4'-biaryl linking characteristic of the acid-catalysed mechanism, 2,4'-biaryl-linking prevails in solvent ethanol, and in acetonitrile, but that in the latter solvent it is slightly replaced, and in acetone largely replaced, by 2, *N'*-semidine linking. We have not an unambiguous interpretation of the latter finding, but a possible picture of it would be that a sufficient return of negative charge from solvent to substrate-nitrogen would favour a transition-state configuration in which the negative nitrogen, rather than the negative *para*-carbon, overlies the centroid of charge in the positive ring, and so leads to 2, *N'*-linking. Another possibility is that the non-catalytic rearrangement of hydrazobenzene, which requires higher temperatures than those of naphthyl hydrazo-compounds, used a homolytic mechanism in solvents of polarity as high as that of acetone. Even the naphthyl compounds may use a homolytic mechanism in hydrocarbon solvents.

The type of theoretical consideration, which we have been using in this Section for the interpretation of orientation, should bear also on rate of rearrangement, though in this field the observations available for discussion are much more limited. However, inasmuch as the activation energy of any reaction is consumed mainly in advancing the leading bond-fission, which in our reaction the polar-transition-state theory assumes to be N-N heterolysis, one can see a reason for the parallelism of rate, in any one mechanism, with the capacity for electron-supply exhibited by the aryl or substituted aryl groups borne by the nitrogen atoms of the hydrazine. The parallelism is shown in the various rate-ordered series of groups, set out in Section 5, for the two-proton, the one-proton, and the no-proton mechanisms of rearrangement (p. 2872).

The hydrazo-compounds, whose rates of rearrangement, by mechanisms kinetically shown to be identical, have been measured in comparative conditions, are those set down in Table 2 (p. 2872). Among these compounds, there was one to which special attention was drawn in Section 5, notwithstanding that its rate fell into line with the already-mentioned parallelism with electron-donation, because the kinetic effect of the substituent, in the positions it occupied in the compound, though qualitatively the same as its effect in other positions, was remarkably large. The common mechanism applying in this comparison was the two-proton mechanism. The parent structure was hydrazobenzene, and the substituent was methyl, two methyl groups occurring in like positions, and in each ring, in each of the isomers compared. Some relative rates of rearrangement were as follows: hydrazobenzene, 1; its 2,2'-dimethyl derivative, 3 or 5; the 3,3'-dimethyl isomer, 6; the 4,4'-isomer, 500 or 800, the alternative figures referring to different solvents. It can be argued that steric hindrance might reduce the rate of rearrangement of the 2,2'-isomer by a factor of the order of 10. However, it remains to be explained why the rate of rearrangement of 4,4'-dimethylhydrazobenzene is so much greater than that of either of its isomers.

The considerations adduced in the preceding discussions of orientation present an

explanation. In the quasi-cationic moiety of the transition state of the two-proton rearrangement of hydrazobenzene, the 4-carbon atom is essentially in carbonium-ionic form [see (Ia)]; but this is the form of a secondary carbonium ion. The same will be true for the two-proton rearrangements of the 2,2'- and 3,3'-dimethyl derivatives of hydrazobenzene. In the transition state of rearrangement of 4,4'-dimethylhydrazobenzene, the corresponding carbon atom is likewise in carbonium-ionic form; but now the form is that of a tertiary carbonium ion. When a tertiary carbonium ion differs from a secondary by a methyl group, as the *t*-butyl carbonium ion differs from the isopropyl, the tertiary is always the more stable. Such an increase, uniquely arising in the 4,4'-dimethyl isomer, in the stability of the carbonium-ionic centre in the transition state of the two-proton mechanism, should manifest itself as an acceleration of the rearrangement. The observed rate in this case is, indeed, outstanding.

(16) *Short Survey*.—So many points have been made in Sections I—15 that we try here to pull them together. Our object has been to examine the present theoretical position of the long-standing problem of the mechanism of the benzidine rearrangement, in view of recent observations, including those recorded in Parts I—XIV.¹ The main groups of observations have been summarised. They relate to the kinetics and products of rearrangement, the products in correlation with kinetics where possible, and both kinetics and products in relation to substrate structure, and to the environmental conditions. Of the three previously propounded theories of the rearrangement which treat the stereochemical side of the problem seriously, *viz.*, the polar-transition-state, the π -complex, and the caged-dissociation theories, the first alone is consistent with the overall observational picture. Furthermore, the new observations allow this theory to be kinetically and stereochemically particularised.

The newer kinetic observations start with Carlin and Odioso's discovery of a case of rearrangement which had a fractional kinetic order in the catalysing acid. This led us to the isolation of one-proton catalysis, and to a proof of the independent concurrence of the two-proton and one-proton mechanisms. This work was guided by successful prediction by the polar-transition-state theory as to effects of structure on kinetic form. The rule is that substituents which supply electrons to the heterolysing bond, and weaken the basic centres, accelerate the one-proton mechanism preferentially.

Polar solvent and salt effects show that the two-proton and one-proton mechanisms develop, in their transition states, very strong polarities, which were not present in their initial states, and stand out above the polarities due to nett ionic charges in both states. Solvent effects show that the no-proton mechanism of the non-catalysed rearrangement in polar solvents at higher temperatures has a similarly highly polar transition state, even though this carries no nett charge.

The two-proton, one-proton, and no-proton mechanisms are all accelerated by substituents which donate electrons to the heterolysing bond. But there are variations according to mechanism. One is noted in the rule given above. Another is that the two-proton mechanism is particularly rate-sensitive to an electron-donating 4-substituent.

The catalyses involved in the two-proton and one-proton mechanisms are wholly of the specific hydrogen-ion type; that is, all the protons concerned are added completely in pre-equilibria. These conclusions are established, alike by the variations of the rates with acidity at high acidities, and by the kinetic effects arising from transferable deuterium in the solvent.

In the two- and one-proton mechanisms, deuteration in the two aromatic positions, from which protons must be lost to form a biaryl bond, affects neither the rate of rearrangement, nor the orientation of biaryl linking; but 2,2'-deuteration does affect the ratio in which the two products of 2,2'-biaryl linking, the diamine and its imine, appear. It is deduced that the aromatic protons are lost after the doubly or singly protonated transition state has been passed, and after the positions of biaryl linking have been determined; and that the aromatic-proton losses are successive, the second competing with loss of

ammonia, where this occurs. In the no-proton mechanism in polar solvents, rearrangement is retarded, the more in the less polar solvents, by prior deuteration in the positions of biaryl linking. It is deduced that the first loss of an aromatic proton has been displaced backwards and upwards on the reaction co-ordinate to the transition state, whilst the second aromatic-proton loss remains a subsequent event, which is still in competition with ammonia loss when this occurs.

The above summary covers our present knowledge, as derived directly from kinetic observations, of the succession of kinetic events. Some confirmatory details follow indirectly from studies of products.

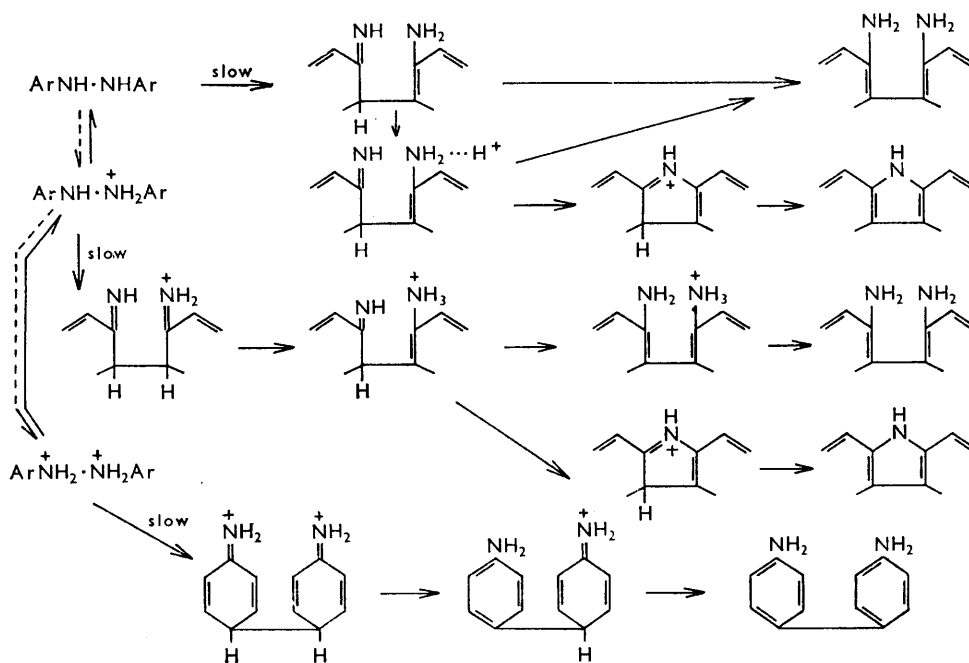
As to products, the trends towards biaryl linking in 2- and 4-positions approximately follow quinonoid stabilities in the benzene and naphthalene series, so pointing to strongly quinonoid bond distributions in transition states. However, the detailed orientational results, for instance, the absence of 2,2'-biaryl linking in the rearrangement of hydrazobenzene, and the absence of 2,4'-linking in that of 1,1'-hydrazonaphthalene or of *N*-1-naphthyl-*N'*-phenylhydrazine, obviously require further interpretation. Dewar's interpretation of this contrast is demonstrably invalid. Dewar's rules for orientation by substituents are equally out of accord with the observations. The following statement is thought to represent the data. A 4-substituent, if strongly electron-donating, leads to 2,*N'*-linking, if not, to 2,4'-linking, and if both strongly donating and attracting (halogens), to both modes of linking; an electron-donating substituent, if at 4, orients linking towards 2, and if at 2, towards 4, with a strength paralleling that of its electron-donation.

The degree of protonation in the mechanism affects the proportions of products from a given substrate. Part of any 2,2'-biaryl linking in the one-proton mechanism is replaced by 4,4'-linking in the two-proton mechanism. This is ascribed to like-charge repulsion during the formation of the two-proton transition state. 2,2'-Linking, which produces a diamine and its imine in the one-proton mechanism, gives the diamine only in the two-proton mechanism. The ring-closure being regarded as heterolytic, and hence as requiring one nitrogen in basic and the other in ammonium form, the second proton of the two-proton mechanism is assumed to exclude imine by destroying the basic centre. Part of any 4,4'-linking in the one-proton mechanism is replaced by 2,2'-linking in the no-proton mechanism. This is ascribed to unlike-charge attraction during the formation of the no-proton transition state. 2,2'-Linking produces both a diamine and its imine, alike in the one-proton and no-proton mechanisms; but in the latter, imine formation is suppressed by added strong bases. It is concluded that, in the no-proton mechanism in protic solvents, adjustments of equivalent protonation of the reacting system, by transfer of protons from, or the sharing of them with, the medium, occur between the first proton-loss in the transition state and the second proton-loss, with which the ammonia loss to give imine is competitive.

The whole body of observations on kinetics and products is considered from the viewpoints of the polar-transition-state, the π -complex, and the caged-dissociation theories. However, the π -complex theory is out of accord with the one-proton mechanism observed in the naphthalene series, with the independent concurrence of the two- and one-proton mechanisms, with specific hydrogen-ion catalysis in the two-proton mechanism, and with kinetic and constitutional effects on products, *inter alia*; and the caged-dissociation theory is in conflict with the one-proton mechanism, with the no-proton mechanism in polar solvents, with salt and polar solvent effects on rate, and with constitutional effects on products, *inter alia*. The polar-transition-state theory has provided all the explanations so far given, but must be pursued in its stereochemical aspects for interpretation of the data still remaining to be explained. These data, which concern constitutional effects on products and rates, are now considered.

The polar-transition-state theory assumes that a leading heterolysis of the N-N bond makes it largely electrostatic and abnormally long and weakly directed, so allowing its replacement by a similarly characterised biaryl or nitrogen-aryl bond, which will finally

shorten to a well-directed covalency. This picture of rearrangement implies, for example, that the transition state of the acid-catalysed rearrangement of hydrazobenzene consists of a dipolar moiety connected by such polar bonds to a positively charged moiety. Electron-delocalisation forces and electrostatic forces jointly determine that the negative charges in the ring of the former are comparably distributed between the 2- and 4- positions, and that the positive charge in the ring of the latter is concentrated on the 4'-position. A displaced convergence of the rings will result, and will lead to 2,4'- and 4,4'-biaryl-linked products. In the examples of 1,1'-hydrazonaphthalene and *N*-1-naphthyl-*N'*-phenylhydrazine, similar considerations require an undisplaced congruence of the interacting rings, and thus require 2,2'- and 4,4'-biaryl-linked products. The interpretation of the finding that an electron-donating 4-substituent, in the order $OR > Alk > Hal$ of orienting power, leads to 2,*N'*-semidine formation is that part of the charge on the 4-position in the positive moiety in the transition state is transferred to the 4-substituent, so enhancing the



displacement accompanying convergence of the rings. Similarly, an electron-donating 2-substituent will withdraw positive charge from the 4-position, thus reducing the displacement on convergence below that characteristic of hydrazobenzene, and in consequence leading to nearly total 4,4'-biaryl linking, if the 4'-position is unsubstituted, or to 4,2'-linking, if the 4'-position bears a substituent less strongly orienting than the 2-substituent. If the 4'-substituent is the more strongly electron-donating, it will act as mentioned above. The same theory of mechanism, applied to non-catalytic rearrangements in polar solvents, describes transition states consisting of positively and negatively charged moieties, with such distributions of charge that the products are broadly similar to those of the corresponding catalytic rearrangements, apart from certain general differences already mentioned.

As to constitutional effects on rate of rearrangement, the general parallelism, in any one mechanism, of rate with electron-release from the aryl or substituted aryl groups of the hydrazine can be understood as an effect of electron-release on the leading heterolysis of the

2900 *Mechanism of Benzidine and Semidine Rearrangements. Part XV.*

rearrangement. The special sensitivity of rate in the two-proton mechanism to an electron-donating 4-substituent can be correlated with the assumed concentration of positive charge on the 4-position in the two-proton transition state.

The kinetic sequences, for the three states of protonation, and for representative modes of biaryl linking, are formulated in the annexed scheme without regard to their stereochemistry. The steps containing the transition states of rearrangement are marked "slow." All other steps are fast by comparison. The stereochemistry of some typical transition states is illustrated in formulæ (I)—(IV) given earlier.

ADDENDUM

Tests for radical intermediates.

Because of the recent advocacy of the caged-dissociation concept of benzidine rearrangements (Section 2), we have tried to detect radical intermediates by electron spin resonance spectroscopy, and by the initiation of polymerisation, in two-proton- and one-proton-catalysed, as well as in non-catalytic, benzidine rearrangements.

Tests by Electron Spin Resonance Spectroscopy.—Runs were carried out in the magnet pole-gap of the spectrometer, with the substrates and in the conditions shown in Table 8.

TABLE 8.
Electron spin resonance runs.

Hydrazo-compound	[Substrate]	Solvent	[HCl]	Temp.
Hydrazobenzene	0.1	" 90% " aq. ethanol	0.2	ca. 0°
1,1'-Hydrazonaphthalene	0.02	" 60% " aq. dioxan	0.01	ca. 0
1,1'-Hydrazonaphthalene	0.002	" 60% " aq. dioxan	0.002	ca. 0
1,1'-Hydrazonaphthalene	0.1	Benzene	None	100

No signal could be detected during the time-course of any of the runs. Signals should have been obtained had radicals, caged or otherwise, been produced in concentrations of $10^{-9}M$. Some tubes were frozen in liquid nitrogen, and the resulting glass was examined in the spectrometer; however, no indication of radicals could be found.

The only previously reported study of the benzidine rearrangement by the use of electron spin resonance spectroscopy is that of Snyder,²⁶ who concluded that the colours sometimes seen during acid benzidine rearrangements—colours such as Dewar attributed to π -complexes^{5a,d}—are due to oxidation of the material.

Tests by Initiation of Polymerisation.—This method is applicable without difficulty to non-catalytic rearrangements, but can be applied to acid-catalysed rearrangements only if the acid is dilute, and then only reliably by nephelometric comparison with a control experiment from which the hydrazo-compound has been omitted. The reason is that the acid itself initiates a slow polymerisation of the monomer additives that we used, *viz.*,

TABLE 9.
Runs with added polymerisable substances.

Solvent	Acid	Temp.	Additive (vol. %)
" 60% " Aq. dioxan	0.01M-HClO ₄	0°	S(5), A(10), M(10), SE(10)
" 60% " Aq. dioxan	0.002M-HClO ₄	0	" " " " " "
Acetonitrile.....	None	70	" S(10), A(10), M(10) "
Benzene	None	100	" " " "

styrene (S), acrylonitrile (A), and methyl methacrylate (M). Styrene-glycerol tristearate emulsion (SE) was also employed, but in this case polymerisation has to be looked for in the oily layer next day, after the layers have separated. Runs were performed, all with

²⁶ Snyder, *J. Amer. Chem. Soc.*, 1962, **84**, 340.

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2901

1,1'-hydrazonaphthalene as substrate, in the conditions recorded in Table 9. No polymerisation accompanied the neutral reactions, and no more accompanied the acid rearrangements than arose in the controls.

Conclusion.—The two tests employed have yielded no indication of the formation of radicals during benzidine rearrangements conducted in representative conditions covering two-proton, one-proton, and non-catalytic mechanisms of rearrangement.

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