Mechanism of Benzidine and Semidine Rearrangements. Part XXV.[1] The Acid-catalysed Disproportionation of Hydrazobenzenes

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Acid treatment of 3,3',5,5'-tetrabromohydrazobenzene resulted in rearrangement (78%) accompanied by disproportionation to azo-compound and fission amine (22%). The proportions of the latter process and the rate of disappearance of the substrate were unaffected by deuteriation of the aromatic rings or by variation in the concentration of the substrate. Similar results were obtained for the disproportionations of 4,4'-dichloro- and 4-acetylamino-substituted hydrazobenzenes. For the former, tracer experiments showed that the azo-compound was formed by oxidation of the substrate rather than by intermolecular recombination of anilino or nitrene fragments, and the percentage of such disproportionation was markedly reduced when the viscosity of the medium was increased by the addition of glycerol.

Rearrangement and disproportionation are considered to be concomitant reactions of different intermediates rather than alternative reactions of a common intermediate. Experiments with e.s.r. and chemically induced dynamic nuclear polarisation (CIDNP) techniques and scavengers suggest that these intermediates are quinonoids.

ACID treatment of many hydrazoarenes results in formation of azo-compounds and fission amines as well as the conventional products of rearrangement. These disproportionation products may predominate (up to 95% total reaction) from 4- or 4,4'-substituted substrates, but are generally formed in negligible quantities from compounds in which these ring-positions are free.[2-4]

All the disproportionations so far studied have the same kinetic order as the concomitant rearrangements, and the two processes are undoubtedly closely related.[5-7] However, despite speculations,[3] nothing is known of the mechanism of the former process. The stoicheiometry suggests the formal redox process (1), but the previously held[8] and recently reiterated[9] view that the rate-limiting step involves bimolecular oxidation of substrate by either a protonated molecule of the hydrazoarene or by a product of rearrangement is not valid,[2,3] for the disproportionations were uniformly of the first order in substrate, and for several examples increase in the initial concentration of the hydrazo-compounds did not increase the percentage of disproportionation.[3,4] We now report a detailed examination of the co-occurring disproportionation–rearrangement of three hydrazobenzenes in an attempt to clarify these matters.

$$2\mathrm{RNH{\cdot}NHR} \longrightarrow \mathrm{RN{=}NR} + 2\mathrm{RNH_2} \qquad (1)$$

R = Substituted phenyl

RESULTS

(a) *Rates and Products from Deuteriated and Isotopically Normal Substrates.*—Product analyses were the means of 3—7 determinations and were reproducible to ±2 units. Rate constants were the means of at least three measurements. Products are assigned as *p*-benzidine, *o*-benzidine,

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2,4′-diaminobiphenyl, *o*-semidine, and *p*-semidine when the rings are linked 4,4′; 2,2′; 2,4′; 2,N′; and 4,N′ (using the numbering of the substrate).

4,4′-*Dichlorohydrazobenzene*. Conditions, 60% dioxan–water (v/v) at 0 °C, 0·913N-perchloric acid, 2×10^{-3}M-substrate: the protium compound gave azo-compound, 42; fission amine, 42; *o*-semidine, 12; and *p*-semidine, 5%; $k_1/\text{s}^{-1} = (2{\cdot}47 \pm 0{\cdot}07) \times 10^{-4}$. The 2,2′,6,6′-tetradeuterio-compound gave azo-compound, 41; fission amine, 39; *o*-semidine, 16; and *p*-semidine, 4%; $k_1/\text{s}^{-1} = (2{\cdot}44 \pm 0{\cdot}09) \times 10^{-4}$.

3,3′,5,5′-*Tetrabromohydrazobenzene*. Conditions, 80% ethanol–water (v/v) at 0 °C, 9·0N-sulphuric acid, $2{\cdot}0 \times 10^{-3}$M-substrate; the protium compound gave azo-compound, 13; fission amine, 9; *o*-benzidine, 3; *p*-benzidine, 7; and 2,4′-diaminobiphenyl, 68%; $k_1/\text{s}^{-1} = (6{\cdot}21 \pm 0{\cdot}09) \times 10^{-4}$. The 2,2′,4,4′,6,6′-hexadeuterio-compound gave azo-compound, 13; fission amine, 11; *o*-benzidine, 2; *p*-benzidine, 6; and 2,4′-diaminobiphenyl, 67%; $k_1/\text{s}^{-1} = (6{\cdot}32 \pm 0{\cdot}10) \times 10^{-4}$.

The proportions of products from the isotopically normal dichloro- and tetrabromo-compounds were unaltered when deuteriated solvents were used, and the products contained no ring-bonded tracer: exchange of deuterium before reaction of the deuteriated substrates was thus ruled out.

4-*Acetylaminohydrazobenzene*. Conditions, 60% dioxan–water (v/v) at 0 °C, 0·007N-perchloric acid, 2×10^{-3}M-substrate: the protium compound gave 38% azo-compound; $k_1/\text{s}^{-1} = (9{\cdot}27 \pm 0{\cdot}06) \times 10^{-4}$. The 2,2′,4′,6,6′-pentadeuterio-compound gave 37% azo-compound; $k_1/\text{s}^{-1} = (9{\cdot}34 \pm 0{\cdot}04) \times 10^{-4}$.

(b) *Effect of Variation of Substrate Concentration on Products*.—4,4′-*Dichlorohydrazobenzene*. Conditions as in section (a). Products at initial substrate concentrations of 0·045, 0·014, 0·0023, and 0·0008M were: azo-compound, 41, 36, 40, 45%; fission amine, 39, 43, 38, 41%; *o*-semidine, 16, 19, 19, 10%; and *p*-semidine 4, 2, 3, 4%.

3,3′,5,5′-*Tetrabromohydrazobenzene*. Conditions as in section (a). Products at initial substrate concentrations of 0·010, 0·002, and 0·0005M were: azo-compound, 14, 14, 17%; fission amine, 13, 14, 12%; *o*-benzidine, 3, 3, 3%; *p*-benzidine, 6, 5, 5%; and 2,4′-diaminobiphenyl, 65, 64, 62%.

Hydrazobenzene. For reaction in 90% ethanol–water (v/v) at 0 °C containing 0·06N-hydrochloric acid, with initial concentrations of substrate 0·198, 0·101, 0·0504, and 0·0270M, the yields of azo-compound were 7·2, 6·4, 7·1, and 7·2%. Reaction in toluene at 0 °C containing 0·35N-hydrogen chloride at initial substrate concentrations of 0·297, 0·198, 0·101, and 0·051M gave yields of azo-compound of 23·5, 3·7, 1·6, and 0·04% respectively.

(c) *Products of Reactions in Solutions of High Viscosity*.—Glycerol replaced part of the aqueous fraction of dioxan–water solvents for certain reactions of 4,4′-dichlorohydrazobenzene and the products were determined at several acidities. Any effects can be attributed to viscosity changes, as the percentage of disproportionation is known [7] to be independent of acidity for the reaction in 60% dioxan–water. With initial substrate concentrations of 4×10^{-3}M, the following results were obtained at 0 °C: M-perchloric acid, viscosity of medium relative to water, percentage azo-product; 0·4, 1·5, 33; 0·4, 8·5, 29; 0·4, 17·0, 25; 1·6, 23·0, 21; 1·5, 30·1, 18; 0·9, 119, 14; and 0·9, 129, 12. A complete product analysis under the third set of conditions gave azo-compound, 25; fission amine, 26; *o*-semidine, 38; and *p*-semidine, 10%. As the proportion of disproportionation was reduced, that of rearrangement was increased.

(d) *Products of Reaction at High Pressures*.—Analysis of products from the 4,4′-dichloro-compound under nominally the conditions described in section (a) at both 3 kbar and atmospheric pressure were carried out by Dr. E. Whalley of the N.R.C., Ottawa. The yields of azo-compound were 26 and 19% respectively.

(e) *Intramolecularity of Azo-formation*.—The mass spectrum of the azo-compound formed from concurrent reaction of equal weights of the 4,4′-dichloro-compound and its tetradeuterio-homologue was compared with that of a mixture prepared from separately performed reactions. The relative abundance of peaks at m/e 250, 251, and 252 were 100, 25, and 90 and 100, 25, and 90 respectively (means of five determinations, all reproducible to ±1 unit). These figures indicate that less than 7% of any azo-compound was derived in the former conditions from coupling of kinetically free anilino or nitrene fragments.

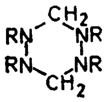
(f) *Trapping Experiments: Cations and Quinonoids*.—A caged dication–amine pair or a free dication (see Discussion section) might react with a scavenger susceptible to electrophilic attack such as anisole, mesitylene, 3,5-dimethoxybenzene, or phenol. Other oxidising species would probably be trapped by hydrazine hydrate, catechol, or ascorbic acid to yield fission amine, but no azo-compound. Quinonoid intermediates could possibly be trapped with cyclopentadiene, maleic anhydride, or tetracyanoethylene.

All these potential scavengers were added in concentrations at least equivalent and usually in ten-fold excess to 4,4′-dichloro-, 3,3′,5,5′-tetrabromo- and 4-acetylamino-substituted hydrazobenzenes and acid-catalysed transformations were carried out as described in section (a). In addition, the additives were employed for the reaction of 4-methoxyhydrazobenzene under previously specified [5] conditions. In all cases except one the percentage of disproportionation was unaffected. In the exception, two unidentified products were isolated from the reaction of 4-acetylaminohydrazobenzene in the presence of tetracyanoethylene. These were traced to reaction of the scavenger with substrate and with rearrangement products rather than with reaction intermediates.

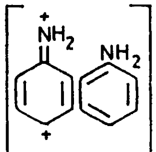
Catechol and phenol would also probably break up any hydrogen-bonded aggregates of the substrate and its protonated forms that could influence kinetics and products. However, the rates of disappearance of the 4,4′-dichloro-compound under the conditions specified in section (a) in the presence of a 6·5 molar excess of catechol and in its absence were $(2{\cdot}47 \pm 0{\cdot}07) \times 10^{-4}$ and $(2{\cdot}43 \pm 0{\cdot}05) \times 10^{-4}\ \text{s}^{-1}$ respectively, and the product distribution was unaffected.

(g) *Trapping Experiments: Radicals*.—Four types of radical scavenger were added to the reactions of 4-chloro- and 4,4′-dichloro-hydrazobenzenes. These were: (i) ferrous and manganous sulphates; (ii) galvinoxyl and diphenylpicrylhydrazyl; (iii) 4,4′-dimethoxydiphenylamine, 2,6-di-t-butyl-4-methoxyphenol, *NN*-diphenyl-*p*-phenylenediamine, 9,10-dihydroanthracene, and 1,4-cyclohexadiene; and (iv) 2-methyl-2-nitrosopropane and t-butylmethylene nitrone. These types could respectively react with radical intermediates by donating electrons, coupling to form neutral species, donating hydrogen atoms, and coupling to form relatively stable radicals.

Although added in quantities varying from equimolar with hydrazo-compound to thirty-fold excess, these scavengers only intervened in two experiments to alter significantly the proportions of azo-compounds (25 and 35% respectively) found in controls. Diphenylpicrylhydrazyl oxidised 4-chlorohydrazobenzene to give 77% azo-compound; and reaction of the 4,4′-dichloro-compound in the presence of t-butylmethylene nitrone reduced the yield of azo-compound to 9% and diminished the recovery of rearrangement products in the same proportion. The latter additive neither reacted with the hydrazo-compound in neutral solution nor with rearrangement products, but a product (80% yield) was recovered from the acid-catalysed reaction as white crystals: m.p. 255° (decomp.) (from acetone); $\lambda_{max.}$ (chloroform) 293 and 250 nm; τ 3·00 (s, 16H) and 4·43 (s, 4H), no hydrogen exchangeable with deuterium; M^+ 528, 4 chlorine atoms present (mass spectrum) (Found: C, 58·7; H, 3·9; N, 10·5; Cl, 26·8. $C_{26}H_{20}Cl_4N_4$ requires C, 58·9; H, 3·8; N, 10·6; Cl, 26·8%). 4-Chloro-*N*-methylaniline has an n.m.r. spectrum with the signal from the aromatic hydrogens almost collapsed to a singlet and all these data are thus consistent with the structure of **1,2,4,5-*tetrakis*-(p-*chlorophenyl*)*perhydro*-1,2,4,5-*tetrazine*** (I); the cracking pattern under election impact can also be rationalised on this basis. The scavenger probably decomposed to form methylene which reacted with the azo-compound to give a product which subsequently dimerised.



(I) (R = *p*-ClC_6H_4)



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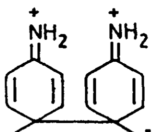

(III)

(h) *E.s.r. and CIDNP Experiments*.—t-Butylmethylene nitrone and 2-methyl-2-nitrosopropane react with certain types of radical to form relatively long-lived radicals that can be detected by e.s.r. spectroscopy.[10] Addition of either scavenger to the acid-catalysed reactions of 4-methoxy- and 4,4′-dichloro-hydrazobenzene however did not produce e.s.r. signals. However, the sensitivity of this probe may have been considerably reduced by the appreciable instability of the scavengers in acidic media.

The chemically-induced dynamic nuclear polarisation (CIDNP) effect is known [11] to cause enhanced absorption or emission lines in the n.m.r. spectrum of products formed from radicals under some conditions. No such phenomenon was observed for the reactions of 4,4′-dichloro-, 4-phenyl-, and 4-chloro-substituted hydrazobenzenes under conditions leading to extensive disproportionation.

(i) *Reactions in Concentrated Sulphuric Acid*.—An intermediate that would normally lose a proton might be stabilised in concentrated acids. However, no n.m.r. signal attributable to the methylene hydrogens of quinonoids could be detected during periods of 24 h from solutions of hydrazobenzene or 4,4′-di-iodohydrazobenzene in concentrated sulphuric acid, although the sensitivity of detection was reduced by a high background in the appropriate region.

The u.v. spectrum of the latter substrate in the same solvent at 20 °C showed, in addition to absorptions attributable to azo-compound, fission amine and iodine, a peak at 318 nm that developed 20 min after mixing and increased five-fold in intensity during 18 h. This peak was replaced by one at 400 nm on addition of *ca.* 6% (v/v) water, and addition of more destroyed the latter peak and gave a spectrum corresponding to a mixture of azo-compound and fission amine. The solution containing the species that absorbed at 318 nm was examined by e.s.r. spectroscopy but no signal was detected. A radical responsible for such absorption can be calculated (from the theoretical maximum molar extinction coefficient) to be present in at least 10^{-7}M, and so should have easily been detected.

No identifiable peak was obtained when similar experiments were carried out with hydrazobenzene.

(j) *Attempts to detect Hydrogen Peroxides*.—An intermediately-formed oxidising species might react with the solvent to form OH^+, $OH\cdot$, or hydrogen peroxide. The first two species should have been scavenged by the previously listed additives, but the last could possibly survive to oxidise substrate. No evidence was found for this compound: addition of potassium iodide–ammonium molybdate to various acid-catalysed rearrangements of the previously detailed substrates or of peroxidase to rearrangements of the 4-acetylamino-compound carried out in buffers at pH 6—7 did not affect the proportions of azo-products.

DISCUSSION

Intramolecularity of Disproportionation.—The absence of cross-product from the concurrent disproportionation of isotopically normal and tetradeuteriated 4,4′-dichlorohydrazobenzene eliminates a mechanism involving fission to anilino- or nitrene moieties (or related species) and intermolecular recombination. No 4,4′-dichloroazobenzene or azobenzene was previously found [4] from acid-promoted decomposition of 4-chlorohydrazobenzene, but here selectivity in recombination between different fission fragments could not be definitely excluded, whereas this possibility could be excluded in our present system.

Preliminary studies with normal and hexadeuteriated 3,3′,5,5′-tetrabromohydrazobenzenes have given the same result. This compound should be favourably disposed for fragmentation with, perhaps, relief of steric strain, and the non-occurrence of fission in this example suggests that intramolecular formation of azo-compounds may be general.

Intermediates in Disproportionation.—The stoicheiometry of equation (1) suggests that a molecule of substrate or its conjugate acid reacts with a species derived from another such molecule. The latter reactant has been suggested to be the oxidising agent that is known to occur transiently during the formation of rearrangement products,[3,6,12,13] and has been suggested to be either a π-complex or a radical.[3,12]

The benzidine rearrangement almost certainly

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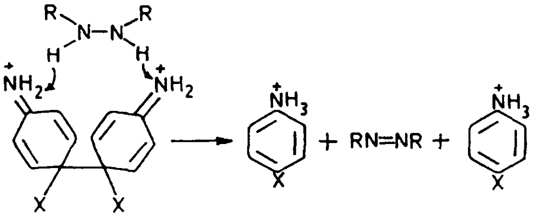
does not generally involve radical–cation pairs or other forms of encumbered radicals as intermediates[2] although such species may occur with esoteric substrates such as 2,2′-hydrazodiphenyl sulphide.[14] Recent studies support this conclusion: generation of arylnitrenes or anilino-radical-ions under various conidtions of solvent and pH either do not give products of benzidine rearrangement or give compounds different from those generated by acid treatment of hydrazo-compounds under similar conditions.[15-19] Nevertheless, the rearrangement could possibly proceed *via* an intramolecular mechanism to yield quinonoid intermediates[2] whereas a concurrently formed intermediate could break down homolytically to yield radicals that reacted with substrate to form disproportionation products. Such a dual pathway of decomposition has been suggested[20] for the intermediates formed in the decomposition of certain peroxides. For the present reactions this type of dual process was made unlikely by the failure to detect radicals by e.s.r. and CIDNP techniques, and is ruled-out by the failure of a wide range of radical scavengers of different types to divert the proportion of reaction leading to disproportionation. The CIDNP technique, in particular, has recently revealed that several rearrangements believed to be heterolytic actually involved radical intermediates.[21-25]

An alternative hypothesis, that at first sight is extremely attractive, is that when rearrangement is inhibited (by, for example, the presence of 4-substituents in the aromatic rings), heterolytic fission of the nitrogen–nitrogen bond of the protonated hydrazobenzene runs ahead of bond-making between the aromatic moieties and an encumbered dication (II) is formed. The dication fragment could then intermolecularly oxidise substrate with the formation of azo-compound and fission amine or the encumbered pair could collapse to rearrangement products. Such a process is however ruled out by the ineffectiveness of large molar excesses of scavengers, that are readily susceptible to oxidation and electrophilic attack, to divert reaction. The intermediate that presumably occurs in disproportionation thus can have neither radical or electrophilic character, yet must specifically oxidise hydrazo-compounds that are present in very low concentrations, whilst having no effect on other potentially oxidisable additives.

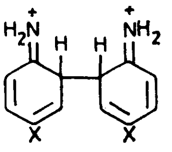
As no concrete evidence has ever been presented for the existence of π-complexes in this type of reaction,[26] the simplest assumption as to mechanism is that disproportionation shares a quinonoid-type intermediate with the concomitant rearrangement mechanism. Attempts to trap quinonoids from reaction mixtures as Diels–Alder adducts failed, but this is inconclusive as the conditions were unfavourable for such reactions. However, the u.v. spectrum of 4,4′-di-iodohydrazobenzene in concentrated sulphuric acid gave a peak a 318 nm, unassignable to reactants or products, that is consistent[27] with a structure (III).

If a quinonoid is an intermediate, the specificity of the reaction with the second substrate molecule may indicate that the reaction is not a redox process in the ordinary sense, *i.e.* where the electrons and protons are transferred separately, but rather involves coupled transfers of hydrogen atoms in a transition state of rigidly defined geometry. Such a process is formally represented in equation (2), and the reacting conformation of the quinonoid could be favoured by electrokinetic forces of attraction between the aromatic rings. Such atom transfers could have very low activation energies as the narrowness of the energy barrier could facilitate tunnelling.



(2)

Mechanism.—It has been suggested[28] that both rearrangement and disproportionation of a particular hydrazo-compound involved the formation of a quinonoid intermediate in the rate-limiting step. For an intermediate such as (IV), proton-loss to give rearrangement products would predominate; whereas if one or two groups that could not be readily expelled were situated at the inter-aryl linkage [*cf.* (V) or (VI)] this reaction would be prevented and the quinonoid would accept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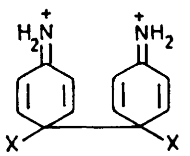
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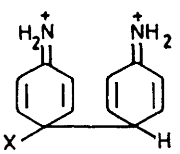
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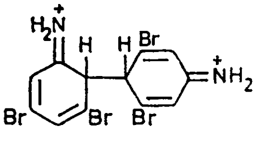
electrons from a substrate molecule in a slower intermolecular process with the concomitant formation of fission amines and azo-compound. If (V) or (VI) were formed irreversibly an increase in the concentration of substrate would not increase the relative proportion of disproportionation, and, consistently, disproportionation is independent of substrate concentration. Also on the basis of this theory, the disproportionation from 4,4′-dichloro- and 4-acetylamino-substituted hydrazobenzenes would arise wholly from 4,4′- and 4,*N*′-linked quinonoids.

A test of this suggestion would be to use a substrate in which rearrangement and disproportionation are in favourable competition, but in which the 2- and 4-ring positions are not blocked, and to attempt to alter the proportions of products by ring deuteriation. One of the few available candidates is 3,3′,5,5′-tetrabromohydrazobenzene, the acid-catalysed reactions of which under non-kinetically controlled conditions have been studied semiquantitatively,[29] and have been shown to lead to about 80% rearrangement and 20% disproportionation. If the intermediates (VII) and (VIII) that we presume lead to 2,4′-diaminobiphenyl (68%) and *p*-benzidine (7%) can be partitioned between rearrangement and disproportionation (the given formulae assume a reasonable but unproven two-proton mechanism), then although ring deuteriation should not affect the rate of disappearance of substrate yet it should increase the yield of disproportionation relative to rearrangement as a C–D bond would be broken in the latter but not in the former process.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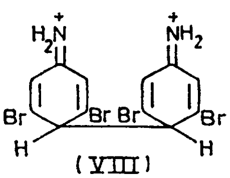
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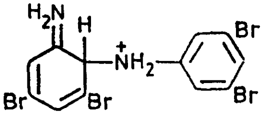
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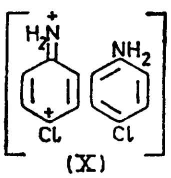
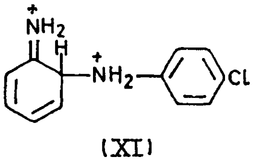
In the event, no isotope effect on either rate or product composition was found. Compound (VII) thus probably goes over entirely to rearrangement products perhaps because a process analogous to equation (2) is not geometrically feasible. Steric interactions could also cause compound (VIII) to rotate rapidly into that conformation with the bulky substituted aryl groups in *anti*-periplanar positions for which the coupled hydrogen atom transfer leading to disproportionation is again impossible. Significant steric interactions between the rings are suggested by the unusually low proportions of *p*-benzidine to 2,4′-diaminobiphenyl, which are in quite an atypical pattern.[2] However, no *o*-semidine is found in this rearrangement and so the disproportionation products may entirely arise from reaction of quinonoid (IX) with unchanged substrate: aromatisation of the intermediate would have to be sufficiently slow as to enable the geometrically favoured intermolecular reduction to predominate over rearrangement. Ring-deuteriation of both the 4,4′-dichloro- and 4-acetylamino-substituted hydrazobenzenes also had no effect on rate or products. Here disproportionation may essentially all have derived from the 4,4′-linked quinonoids that are less bulkily substituted and can maintain a conformation suitable for reaction (2) to take place.

Reaction of the 4,4′-dichloro-compound under high pressure increased the yield of azo-compound from 19 to 26% but the significance of this change is uncertain in view of the difficulty of temperature control in the high-pressure run. The applied pressure only increased the viscosity of the reaction medium several-fold whereas increases of 100-fold were achieved by addition of glycerol and under the latter conditions a marked reduction (33—12%) in the percentage of disproportionation occurred. This significant change may have arisen because the rate of bimolecular reaction to lead to disproportionation of the species (V; X = Cl) would have been reduced some 100-fold by the viscosity change [30] and so the usually negligible breakdown of the 4,4′-linked quinonoid to the caged pair (X)and thence collapse to the *o*-semidine *via* the formation of (XI) may have intruded. The rate of the latter intramolecular sequence would have been little effected by the increase in viscosity.

We suggest that, in general, rearrangement and disproportionation may be concomitant reactions of different intermediates as discussed in the above examples, rather than alternative pathways from a common quinonoid intermediate.


(X)


(XI)

The relative proportions of the pathways to rearrangement and disproportionation of hydrazobenzene itself were unaltered by an increase in concentration of the substrate when aqueous ethanol was solvent (*ca.* 7% azo-compound was found in all conditions), but when toluene was used a strong dependence resulted: increase in the concentration of hydrazobenzene from 0·051 to 0·297M led to an increase in the percentage of azo-product from 0·04 to 23·5%. Proton loss from quinonoid intermediates to give rearrangement products would be more difficult in aprotic than in protic media and capture (perhaps rate-limiting) by unchanged substrate to give disproportionation products could

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[29] R. B. Carlin and G. E. Foltz, *J. Amer. Chem. Soc.*, 1956, **78**, 1992.

[30] Y. Schaafisma, A. F. Bickel, and E. C. Kooyman, *Tetrahedron*, 1960, **10**, 76.

then become a favoured reaction. Comparisons of the proportions of disproportionation and rearrangement from isotopically normal and deuteriated hydrazobenzene and kinetic studies of the reactions in aprotic media are in progress.

EXPERIMENTAL

Preparations.—All m.p.s are uncorrected and agreed ±1 °C with literature values unless otherwise specified.

Asymmetrical azo-compounds were prepared [31] by reaction of nitrosobenzene and the appropriately substituted aniline, and were purified by chromatography on alumina with benzene as eluant, followed by recrystallisation from the same solvent or from aqueous ethanol. 4-Acetylaminoazobenzene (m.p. 152°; yield 70%); 4-methoxyazobenzene (m.p. 55°; yield 25%); and 4-chloroazobenzene (m.p. 89°; yield 70%) were thus prepared.

4,4′-Dichloroazobenzene (m.p. 187°; yield 80%) was made by oxidation [32] of 4-chloroaniline with freshly prepared [33] manganese dioxide.

3,3′,5,5′-Tetrabromoazobenzene was prepared by the sequence: bromination of 4-nitroaniline to give 2,6-dibromo-4-nitroaniline (m.p. 202—205°; yield 40%), deamination [29] to give 3,5-dibromonitrobenzene (m.p. 105°; yield 52%), reduction with iron in dilute sulphuric acid [34] to give 3,5-dibromoaniline (m.p. 56°; yield 40%), and reductive coupling [35] to give the azo-compound (m.p. 246°; yield 89%).

Hydrazobenzenes were prepared by conventional reductions of the azo-compounds. In this way, 3,3′,5,5′-tetrabromohydrazobenzene, m.p. 183°; 4,4′-dichlorohydrazobenzene, m.p. 130°; 4-acetylaminohydrazobenzene, m.p. 152°; 4-chlorohydrazobenzene, m.p. 89°; 4-methoxyhydrazobenzene, m.p. 78°; 4,4′-di-iodohydrazobenzene, m.p. 140°; and hydrazobenzene, m.p. 126°, were obtained.

2,4,6-Trideuterioaniline that was deuteriated to the extent 90, 100, and 90% in the three positions; 2,6-dideuterio-4-chloroaniline to 85% in each position; and 2,6-dideuterio-4-acetylaminoaniline to 81% in each position were all prepared by adaptions of a published method [36] and assayed for label by n.m.r. spectroscopy. 2,4,6-Trideuterionitrosobenzene was prepared by reduction of 2,4,6-trideuterionitrobenzene.[37] 3,3′,5,5′-Tetrabromo-2,2′,4,4′,6,6′-hexadeuterioazobenzene (m.p. 246°; yield 70%) was prepared from the corresponding deuterioaniline by oxidation with manganese dioxide. N.m.r. analysis indicated 100% deuterium at the 4,4′-positions and 90% at the 2,2′- and 6,6′-positions.

The ring-deuteriated 4,4′-dichloro- and 4-acetylamino-compounds were prepared from the deuteriated amines by adaption of the method used for the isotopically normal compounds.

Kinetic Methods.—These are described in previous Parts. Typically, aliquot portions were quenched in 2N-sodium acetate (15 ml) and unchanged substrate was was titrated with Bindschledler's Green. The titrant was prepared according to a recipe [38] except that after the addition of zinc in the reduction step, a ten-fold increase in the specified quantity of hydrochloric acid was added. If the published procedure was followed an impure brown powder rather than shiny green crystals was obtained.

(c) *Product Analyses.*—Methods for the analyses of products of reactions of 4,4′-dichloro- and 4-acetylamino-substituted hydrazobenzenes have been described.[5-7] Products of reactions of the tetrabromo-compound were extracted from the basified solution, separated by t.l.c. on Merck silica gel H (0·04 cm) with methanol–benzene (0·4: 99·6 v/v) as eluant, extracted from the plate, and assayed spectrophotometrically. Assignments of structures of the isomeric products by u.v. spectra and the colour reactions obtained with various spray reagents [1] were in agreement with the previous conclusions. The products were azo-compound, R_F 0·82; m.p. 247°; $\lambda_{max.}$ (chloroform) 447 nm (ε 447): fission amine, R_F 0·42; m.p. 56°; $\lambda_{max.}$ (methanol) 307 nm (ε 1238); *o*-benzidine, R_F 0·65; m.p. 162°; $\lambda_{max.}$ (methanol) 307 nm (ε 4640): *p*-benzidine, R_F 0·28; m.p. 227° (lit.,[39] 242°); $\lambda_{max.}$ (methanol) 305 nm (ε 4220); and 2,4′-diaminobiphenyl, R_F 0·17; m.p. 177° (lit.,[39] 180°); $\lambda_{max.}$ (methanol) 305 nm (ε 896).

High-pressure Experiment.—The solution of 4,4′-dichlorohydrazobenzene was cooled to 10 °C before compression and allowed to warm by *ca.* 10 °C during the 3—4 min that were required to achieve 3 kbar pressure. The acid concentration (2·30M-perchloric acid) was so chosen that the half-life of the reaction was *ca.* 1·5 h.

Experiments with Scavengers.—These were carried out in three-necked flasks, the compartments of which contained the substrate, the catalysing acid, and the trapping agent respectively. The last was generally used in 10—100-fold molar excess over the substrate. The vessel was degassed and filled with nitrogen by a four-fold cycle of freezing and evacuation, and the three solutions were simultaneously mixed and the reaction carried to completion. Controls were performed without the scavenger.

E.s.r. Studies.—Cooled deoxygenated solutions of the catalysing acid and the hydrazo-compound were mixed in the probe of the spectrometer and scanned at 5 min intervals during 30—60 min. A modified Varian 4500 spectrometer was used with a 100 kHz modulation unit. Radical concentrations down to 10^{-9}M were detectable in controls.

(g) *CIDNP Studies.*—Measurements were carried out under nitrogen with a Varian 100 MHz machine. Scans were carried out every min across the region of the resonance bands of aromatic hydrogens.

Reactions in Concentrated Acid.—N.m.r., e.s.r., and u.v. measurements were made on hydrazobenzene and its 4,4′-di-iodo-homologue directly after these compounds were added to concentrated sulphuric acid, and for periods up to 24 h.

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