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Benzidine Rearrangement. 14. The Nitrogen Kinetic Isotope Effect in the Acid-Catalyzed Rearrangement of Hydrazobenzene[1,2]

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Abstract: Rearrangement of hydrazobenzene was carried out at 0 °C in ~75% aqueous ethanol which was 0.1 M in HCl. Rearrangement products were isolated at 10, 20, 30, and 100% extents of rearrangement and converted into nitrogen gas whose $^{29}N_2/^{28}N_2$ contents were determined by isotope-ratio mass spectrometry. By this means the rearrangement was found to have a kinetic nitrogen isotope effect (k^{14}/k^{15}) of 1.0203 ± 0.0007, demonstrating that breaking of the N–N bond in this two-proton rearrangement is part of the rate-determining step. The result is inconsistent with two mechanisms of the rearrangement which are found in the literature: the rate-determining formation of $C_6H_5N^+H_2N^+H_2C_6H_5$ followed by its rapid rearrangement; and rate-determining second protonation at C-1 carbon atom followed by the rearrangement of the ring-protonated dication. The isotope effect result is consistent with two pathways but cannot distinguish between them: preequilibrium diprotonation at the two nitrogen atoms followed by the rate-determining rearrangement of $C_6H_5N^+H_2N^+H_2C_6H_5$; and the rate-determining concerted scission of the N–N bond and approach of the second proton to $C_6H_5N^+H_2NHC_6H_5$, the second proton being almost but not completely transferred in the transition state.

Although a great deal is known and has been written about the acid-catalyzed benzidine rearrangements,[5] a completely satisfying understanding of their mechanisms is still not at hand. It is recognized and now universally accepted that two classes of acid catalysis exist, commonly called one-proton and two-proton rearrangements. These terms signify that some rearrangements are kinetically first order while others are second order in acid. It is also recognized that a particular rearrangement may at low acidities exhibit first order, and at higher acidities exhibit second-order acid catalysis. All rearrangements, of course (at least, to date), are first order in hydrazoaromatic.

For some years these kinetic features were described with widespread, but not total, acceptance by eq 1–4.

$$\mathrm{ArNHNHAr} + \mathrm{H}^+ \rightleftarrows \mathrm{ArN^+H_2NHAr} \quad \text{(fast)} \qquad (1)$$

$$\mathrm{ArN^+H_2NHAr} \rightarrow \mathrm{product}^+ \quad \text{(slow)} \qquad (2)$$

$$\mathrm{ArN^+H_2NHAr} + \mathrm{H}^+ \rightleftarrows \mathrm{ArN^+H_2N^+H_2Ar} \quad \text{(fast)} \qquad (3)$$

$$\mathrm{ArN^+H_2N^+H_2Ar} \rightarrow \mathrm{product}^{2+} \quad \text{(slow)} \qquad (4)$$

The equations require that the protonations of steps 1 and 3 are fast and reversible, a conclusion which had been developed principally from the solvent-isotope work of Banthorpe, Hughes, and Ingold,[5c] and that rearrangements involve the rate-determining scission of the N–N bond. The major unsolved question in benzidine rearrangements appeared for a long time to be, therefore, how steps 2 and 4 occurred; that is, how indeed the mono-N-protonated and di-N,N′-protonated molecules underwent intramolecular rearrangement. It was the seeking of answers to this question which culminated in the several theories of rearrangement; the polar transition state theory,[5c] the π-complex theory,[5a,b] and the cation-radical theory, among which the first appeared to hold the field.[5d,h]

There were some early critics of the idea that the second protonation at nitrogen (step 3) would be fast and reversible. Dewar had incorporated in his original π-complex theory of rearrangement a slow, rate-determining approach of the second proton , an approach which caused a monocationic π complex to reorganize into the product.[5a] Lukashevich,[6] on the basis that, while a hydrazobenzene monochloride was isolable a dihydrochloride was not, also proposed that a second protonation could not occur, but instead that the second proton caused rearrangement to occur during the progress of its approach to the monocation. These proposals were for the most part critically rejected, the rate-determining protonation one because there was no supporting kinetic evidence,[5c,d,7] and the π-complex one because it contradicted in some of its other aspects other features of benzidine rearrangements.[5c,d] More definitive proposals of slow proton transfer for the second protonation were made by Cohen and Hammond[8] and Vecera, Synek, and Sterba.[9] In the former case the rearrangement of hydrazobenzene was classified, from work with buffered solutions, as exhibiting general rather than specific acid catalysis. In the latter case the option for slow proton transfer was made from the effects of acidity and solvent on the kinetics and composition of products of rearrangement of hydrazobenzene. Both groups acknowledged, also, that it was not kinetically possible to distinguish between two processes, eq 5 and 6 and eq 7.

$$\mathrm{C_6H_5N^+H_2NHC_6H_5} + \mathrm{HA} \rightarrow \mathrm{C_6H_5N^+H_2N^+H_2C_6H_5} \quad \text{(slow)} \qquad (5)$$

$$C_6H_5N^+H_2N^+H_2C_6H_5 \rightarrow \text{products (fast)} \quad (6)$$

$$C_6H_5N^+H_2NHC_6H_5 + HA \rightarrow \text{products (slow)} \quad (7)$$

Cohn and Hammond were of the opinion, though, that the concerted process (eq 7) is improbable and concluded that the N,N′-diprotonated hydrazobenzene is a real intermediate. On the other hand Vecera and co-workers concluded that scission of the N–N bond was rate determining and, therefore, seemingly opted for the concerted process.

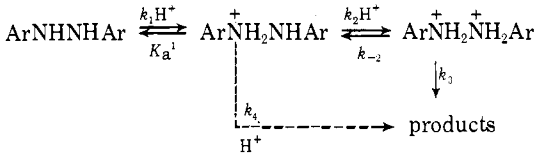
For years, because of the lack of convincing evidence in their favor, the case for rate-determining second protonation, and the possibility that N–N bond scission was fast, received only passing attention by other workers. Several developments have recently brought these views into focus again. On the one hand, Banthorpe has found several examples of two-proton rearrangement in which solvent isotope effects point to the second proton's addition as being rate determining, while on the other hand a number of proposals have appeared for the second proton's addition to ring carbon (ipso addition) rather than to the second nitrogen atom. Addition to ring carbon is believed to be slow.

The analysis of solvent-isotope effects is an important criterion in reaching conclusions on whether the addition of the second proton in a two-proton rearrangement is an equilibrium or slow, rate-determining process. The standard for the rate enhancement per proton in the equilibrium process is established from genuine one-proton rearrangements. Banthorpe has established k_{D_2O}/k_{H_2O} values of 1.9, 2.2, and 2.3, respectively, for one-proton rearrangements of 2,2′-dimethoxy-,[10] 2,2′-diiodo-,[10] and *N,N*′-dimethylhydrazobenzene,[11] and 2.3 for *N,N*′-dimethylhydrazo-1-naphthalene.[11] On these bases a two-proton rearrangement is considered to have both protons preequilibrated if it shows a solvent isotope effect of between 4.0 and 5.3. In this context the two-proton rearrangements of 2,2′-dibromo-,[10] 2,2′-dichloro-,[10] 4-chloro-,[10] and *N*-acetylhydrazobenzene[11] had solvent-isotope effects of 2.0, 2.3, 3.0, and 3.1, respectively. Banthorpe considers, therefore, that in these four cases the addition of the second proton is slow and characterized with k_{D_2O}/k_{H_2O} values of 0.7–1.0. Banthorpe points out that these values represent kinetic isotope effects whose small magnitudes would result from the second proton's having been almost completely transferred in the transition state. In contrast with these four cases, *N*-methylhydrazobenzene ($k_{D_2O}/k_{H_2O} = 4.0$) is considered to be a two-proton equilibrium case, similar to that of the original case, hydrazobenzene with $k_{D_2O}/k_{H_2O} = 4.8$.[5c] It is implicit in Banthorpe's work that the four slow proton transfer cases are the unusual ones, resulting from the particularly weak basicity of the four hydrazoaromatics, the larger known number of other two-proton cases being regarded as prerearrangement equilibrium protonations.

All of these data were obtained from rearrangement in 60% dioxane-water. In a similar approach Bunton and Rubin,[12] working with water solutions, however, measured the solvent-isotope effects for hydrazo-*o*-toluene (under one-proton conditions) and hydrazobenzene (which is a two-proton rearrangement in water, too). The values of k_{D_2O}/k_{H_2O} were 2.33 and 4.0, respectively. Bunton and Rubin feel that the value for hydrazobenzene is low; that is, in order to have both protons equilibrated before rearrangement k_{D_2O}/k_{H_2O} would, in their view, have to be about 5.4. In the rearrangement of hydrazobenzene in water, therefore, the addition of the second proton is believed to be slow and to be almost completely transferred in the transition state, in contrast with the interpretation of rearrangement in aqueous dioxane,[5c] but in analogy with the other cases reported recently by Banthorpe.[10,11] To some extent, then, conclusions based on solvent-isotope effects are predicated on what value is taken as the norm for the rate enhancement per proton.

Bunton and Rubin support their contention about hydrazobenzene with other data, however. In strong aqueous acid ($-H_0' \simeq 1.0$–1.2) hydrazobenzene is extensively monoprotonated and the dependence of rearrangement on acidity shifts from second toward first order. Analysis of the kinetics over a range of acidities was carried out, therefore, and rate constants for Scheme I were calculated with the aid of an estimate of the second (hypothetical) equilibrium constant K_a'' (10^6–10^7) based on equilibrium data for phenylhydrazine and aniline. In this way Bunton and Rubin estimate that k_3 would have to be in the range 10^8–10^9 s^{-1} if the second protonation was an equilibrium process. This in turn would require k_{-2} to be greater than 10^8–10^9 s^{-1}, a value Bunton and Rubin consider too large to be probable. Therefore the rearrangement is considered to follow the concerted process (k_4).

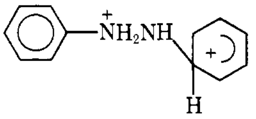
Scheme I



Analogous analyses were made for the rearrangements of hydrazo-*o*-toluene and hydrazo-*o*-anisole which tend toward two-proton cases at higher acidities, and again values of k_{-2} were computed to be unacceptably large if preequilibrium were to be established.

Thus for these three hydrazo compounds the two-proton rearrangement in aqueous acid is believed to be characterized by a rate-determining addition of the second proton, either to nitrogen with concerted N–N bond breaking or to ring carbon before N–N bond breaking.[12]

Protonation at a ring carbon atom has been advocated only in recent years.[13] Its most detailed exposition has been presented by Olah,[13d] and in this it is proposed that the second proton in the rearrangement of hydrazobenzene adds not to nitrogen but to the C-1 position (**1**). Addition of this proton is believed to be rate determining,[13d] and to be followed by the rearrangement step which is looked upon as an intramolecular aromatic alkylation reaction. Although some examples of ring-protonated aromatic amines are known, among them 4,4′-diprotonated benzidine,[13d] there is, of course, no direct evidence whatsoever, as yet, that hydrazobenzene (or any other hydrazoaromatic) undergoes ring protonation prior to or during rearrangement. All proposals for ring protonation are, in that sense, speculative, and based primarily on the feeling that protonation at the second nitrogen atom is highly improbable.



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In particular, rearrangement of hydrazobenzene in D_3O^+ failed, apparently, to place deuterium in any of the ring positions (2, 3, 5, 6).[13d] Whether or not deuterium exchange occurred at the 4 position could not be established, of course, because only the product, benzidine, was examined. The conclusion reached by Olah about these results is that protonation is specific at the 1 position, and, as a corollary to this, N–N bond breaking cannot be part of the rate-determining process. This is a distinction of considerable importance from the process of bond breaking concerted with approach of the second proton to the second nitrogen atom.

The foregoing analysis has been given in some detail so as to emphasize how difficult—indeed impossible—it is to settle the bond-breaking process with hydrogen isotope effects. With this in mind we have examined the kinetic nitrogen-isotope effect for the rearrangement of hydrazobenzene. Investigations of nitrogen-isotope effects are only sparsely recorded in the literature,[14] and have been concentrated on C-N bond breaking in elimination reactions among quaternary ammonium ions. The effects are quite small; but a kinetic isotope effect, say, of $k^{14}/k^{15} = 1.02\text{-}1.03$ is considered to be firm evidence for substantial weakening of the bond to nitrogen in the transition state.[15] As far as we know, no investigation of a kinetic isotope effect for the breaking of an N-N bond has been reported.

Results and Discussion

Our first approach was to carry out traditional kinetics with ordinary hydrazobenzene and fully labelled hydrazobenzene, $C_6H_5{}^{15}NH{}^{15}NHC_6H_5$. We anticipated that the chances of detecting an isotope effect by this method would be remote, but the rate of rearrangement under specific conditions was to be needed in any case later for taking samples for the mass spectrometric method. Rearrangements were carried out at 0 °C in approximately 75% aqueous ethanol which was 0.1 N in HCl. Solutions were kept at an ionic strength of 0.4 with LiCl. Rearrangement of $C_6H_5NHNHC_6H_5$ (five runs) gave a pseudo-first-order rate constant $10^3k^{14} = 7.0 \pm 0.58$ min^{-1}, while rearrangement of $C_6H_5{}^{15}NH{}^{15}NHC_6H_5$ (three runs) gave $10^3k^{15} = 6.53 \pm 0.46$ min^{-1}. These results gave an isotope effect k^{14}/k^{15} of about 1.07 but it was apparent that the accuracy of the rate measurements was too low to allow much reliance on the results.

In view of this we turned to another traditional but reliable technique, isotope-ratio mass spectrometry. Rearrangement of ordinary hydrazobenzene, i.e., containing the natural abundance of ^{15}N, was carried out on a large scale under the same conditions and concentrations of the kinetic runs. The rearrangement was interrupted at specifically chosen times to give products of 10, 20, 30, and 100% rearrangement, and the isotopic abundancy ($^{29}N_2/^{28}N_2$) in the rearrangement products was determined. From these data the ratio k^{14}/k^{15} was calculated.

Rearrangement of hydrazobenzene gives two major products, benzidine and diphenyline, in the approximate ratio 70:30. It is well known that these products are formed by the same kinetic pathway, and therefore we chose for most of our work not to separate the products, but to make most of the nitrogen analyses on the mixtures. Thus, from five identical runs a total of 20 samples was obtained as five sets of 10, 20, 30, and 100% extents of rearrangement. In one run, however, each of the four mixtures was divided into halves, and the individual products in one half were separated by preparative TLC. This gave four samples of benzidine which were also used for nitrogen analysis. Unfortunately, not enough diphenyline was formed to allow of its analysis, too. The results are given in Table I. From successful analyses of 17 mixtures of rearrangement products we have obtained a kinetic isotope effect (k^{14}/k^{15}) of 1.0203 ± 0.0007, while from analysis of the four samples of benzidine we have obtained 1.0205 ± 0.0037. We feel that results for mixed products and benzidine are entirely self-consistent, the larger error of the latter arising from the smaller number of samples available.

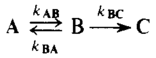
Since some of the mechanistic alternatives discussed above involve rapid preequilibria, it is necessary to consider briefly their effect on the observed isotope effect. In a two-step mechanism involving a rapid preequilibrium (Scheme II), i.e.,

Table I. $^{14}N/^{15}N$ Ratios and Kinetic Isotope Effects for the Rearrangement of Hydrazobenzene at 0 °C

Expt[a]	Extent of reaction, %	$^{14}N^{14}N/^{15}N^{14}N$[b]	$(k^{14}/k^{15} - 1)100$
1/4	100	135.05	
2/4	100	135.03	
3/4	100	135.01	
4/4	100	134.97	
5/4	100	135.01	
3/1	9.6	137.56	2.02
4/1	9.5	137.63	2.07
5/1	9.3	137.65	2.08
2/2	20.1	137.35	1.96
3/2	19.3	137.43	2.02
4/2	19.9	137.43	2.03
5/2	19.5	137.56	2.14
1/3	30.1	137.24	2.01
2/3	29.2	137.14	1.91
3/3	29.4	137.39	2.14
4/3	29.5	137.27	2.01
5/3	29.4	137.16	1.93
1/1[c]	10.0	136.96	1.54
2/1[c]	9.3	137.03	1.59
1/2[c]	20.0	135.69	0.57
1a/4[d]	100	134.68	
1a/1	10.0	137.36	2.13
1a/2	20.0	137.50	2.38
1a/3	30.1	136.46	1.65

[a] The designations mean, for example, that 1/4 is run 1 and sample 4 (i.e., complete reaction). [b] Ratios relative to a standard nitrogen source whose $^{14}N^{14}N/^{15}N^{14}N$ ratio was arbitrarily chosen as 136.5. [c] These runs are separated from the rest since they are obviously in error, possibly from contaminations, and were not used in calculating the isotope effect. [d] Runs 1a are those in which benzidine was separated from the products.

Scheme II



$$A \underset{k_{BA}}{\overset{k_{AB}}{\rightleftharpoons}} B \xrightarrow{k_{BC}} C$$

where $k_{AB}, k_{BA} \gg k_{BC}$, the measured isotope effect $\alpha_m = (k^{14}/k^{15} - 1)$ is a function of the kinetic isotope effect of the rate-determining step α_{BC}, the equilibrium isotope effect of the preequilibrium $(\alpha_{AB} - \alpha_{BA})$, and the chemical equilibrium constant of the preequilibrium K_{BA}.

$$\alpha_m = \frac{(\alpha_{AB} - \alpha_{BA})}{1 + K_{BA}} + \alpha_{BC} \qquad (8)$$

Depending on the magnitude of K_{BA}, the observed isotope effect may therefore contain a contribution from the preequilibrium isotope effect. An estimate for the preequilibrium isotope effect in the present case may be obtained from the work of Urey,[16] who studied the reaction

$$^{15}NH_3(g) + {}^{14}NH_4{}^+(sol) \rightleftharpoons {}^{14}NH_3(g) + {}^{15}NH_4{}^+(sol) \qquad (9)$$

and found an equilibrium isotope effect of about 1.023. The heavy nitrogen isotope is concentrated in the ammonium ion. It may be assumed, by analogy, that this is also the case in the protonation of hydrazobenzene. The preequilibrium isotope effect thus favors the ^{15}N species; the kinetic isotope effect, the ^{14}N species. Expressed in the language of eq 8 this means that $(\alpha_{AB} - \alpha_{BA}) < 0$. The measured isotope effect α_m, which is positive, therefore must result from the kinetic isotope effect of the rate-determining step and, in fact, represents a lower limit for this value.

Under these conditions it is very difficult to determine the exact extent of bond weakening which corresponds to a mea-

Table II

% reaction based on k	% reaction based on product				
	Run 1	Run 2	Run 3	Run 4	Run 5
10	9.9	9.3	9.6	9.4	9.3
20	20.0	20.2	19.3	19.9	19.5
30	30.1	29.2	29.4	29.5	29.4

sured isotope effect of 2%, but this is not critical to our argument. A reasonably reliable estimate could only be obtained from a detailed model calculation. The theoretical maximum isotope effect corresponding to complete rupture of the N-N bond might be expected to be between 4 and 5%. This rough estimate is based on Saunders'[17] calculations for C-N bond rupture and a comparison of C-N and N-N bond force constants.[18]

We conclude therefore that the rearrangement of hydrazobenzene under the conditions described has a significant kinetic nitrogen isotope effect of 1.02, and we consider this to demonstrate that the N-N bond is broken during the rate-determining step of the rearrangement. We believe that this is the first time that this definition of the rate-determining step can be made with confidence. It is now possible to focus attention on mechanisms consistent with this definition and to winnow out those which are not.

One earlier and one recent proposal are inconsistent with our finding.

The first proposal is by Cohen and Hammond. Slow formation of the N,N′-diprotonated intermediate and its fast rearrangement (eq 5 and 6) are unacceptable, since now the breaking of the N-N bond comes after the rate-determining step.

The more recent proposal is Olah's for protonation of the C-1 carbon atom (**1**). In this proposal protonation at C-1 is considered to be rate determining, and the intermediate **1** is considered to be a real intermediate. Implicit in this proposal, therefore, is the rapid rearrangement of the intermediate in a non-rate-determining way. This proposal is inconsistent with the kinetic nitrogen isotope effect, and therefore is not valid.

Beyond this stage we arrive at the two acceptable pathways involving protonation at nitrogen, and cannot distinguish between them with the ^{15}N data. These are the concerted process (eq 7) and the long-known rapid equilibration process (eq 3 and 4). In our view a decision made at this time between these processes is going to be a personal one depending on how one evaluates the hydrogen isotope effects and also Bunton's estimates of rate constants. Whether or not it will be possible to remove this remaining question incontrovertibly appears at this stage to be doubtful.

Experimental Section

Chemicals. Technical grade benzene was refluxed over and distilled from CaH_2. Ethanol (95%) was used without further purification. Aniline was freshly distilled. [^{15}N]Aniline was obtained from Koch Isotopes, Cambridge, Mass., and used without distillation. Titanous chloride was a commercial 20% solution from La Motte Chemical Co. and was used to make 0.01 N solutions which were stored under nitrogen and standardized daily. Active MnO_2 was prepared from manganous sulfate.[19] Aniline (and [^{15}N]aniline) was oxidized to azobenzene with MnO_2.[20] For the mass spectrometric work zone-refined unenriched azobenzene was used (Aldrich Chemical Co.). The azobenzene was reduced to hydrazobenzene with zinc and NH_4Cl in aqueous acetone,[21] and this was recrystallized from aqueous ethanol. Bindschedler's green was prepared as described.[22]

Kinetic Method. The kinetic experiments were carried out at 0 °C as described earlier.[23] The solutions, however, were made by dissolving the reactants in 75 mL of 95% ethanol and diluting to 100 mL with water. Such a solution of hydrazobenzene and another of hydrogen chloride and LiCl were kept until they reached the temperature of an ice slurry and then mixed to give the desired reaction solution. The kinetic data were plotted but also analyzed by a standard computer program to give the first-order rate constants and standard deviations.

Samples for Mass Spectrometry. Samples were obtained from large-scale rearrangements carried out under the same conditions as those of the kinetic runs, but using only unenriched hydrazobenzene. The times of taking samples and quenching the rearrangement were calculated from the known first-order rate constant, so as to provide products from 10, 20, and 30% extents of rearrangement. The sample for complete rearrangement was obtained by allowing reaction to go overnight. The procedure is illustrated as follows. A solution of 2.208 g (0.012 mol) of hydrazobenzene in a mixture of 450 mL of 95% ethanol and 150 mL of water was stirred in an insulated bath of ice slurry until the temperature reached 0 °C. The flask was equipped so as to allow expulsion of large aliquots by applying nitrogen pressure. A solution of 15.42 g (0.364 mol) of LiCl in a mixture of 51 mL of 2.353 N alcoholic HCl, 399 mL of ethanol, and 150 mL of water was similarly cooled. The two solutions were then mixed quickly and three successive aliquots of 500, 250, and 190 mL were pumped out after intervals of 14.7, 31.4, and 50.4 min, respectively, into measuring cylinders containing respectively 25, 13, and 10 mL of saturated KOH solution. The solution remaining in the reaction flask was kept overnight for taking the complete-reaction sample. The unrearranged hydrazobenzene in an alkaline, quenched aliquot was next oxidized to azobenzene by bubbling oxygen through the solution. Oxidation was monitored by periodic TLC tests for hydrazobenzene, but bubbling of oxygen was continued for some time aftor the indicated completion of oxidation. The alcohol was then removed in a rotary evaporator and the organic residue was extracted with ether. The dried solution was then evaporated to give a tared residue. The residue was redissolved in dry ether into which dry HCl was bubbled for 10 min to precipitate the dihydrochlorides of the rearrangement amines, leaving in solution the azobenzene resulting from oxidation of unrearranged hydrazobenzene. The aliquot from complete rearrangement was worked up in a similar way except that the alkaline oxidation stage was omitted. This procedure was repeated five times, giving a total of 20 samples of the rearrangement diamine dihydrochlorides. The hydrochloride mixture was weighed in every case and closely fitted the extent of reaction calculated from the rate constant at 0 °C. The data are given in Table 11. Part of each of the four samples from run 1 was treated with KOH and extracted with ether to give a mixture of the rearrangement diamines. Each mixture was subjected to preparative TLC and the benzidine band was removed and converted into its dihydrochloride in the usual way. In addition to benzidine the TLC showed the band for diphenyline and several bands of minor components. The major products of rearrangement of hydrazobenzene are known to be benzidine and diphenyline, and it is known also that trace amounts of the other possible rearrangement products are also formed and are detectable only by chromatography.[24] Benzidine and diphenyline needed for monitoring the TLC work were obtained from column chromatographic separations of larger scale rearrangements. It should be noted also that control experiments with mixtures of azobenzene and benzidine showed that precipitation of the benzidine from ether with HCl gas was clean, and not contaminated with azobenzene.

By these procedures 20 samples of mixtures of rearrangement amine hydrochlorides and four samples of separated benzidine dihydrochloride were obtained for mass spectrometric measurement of their $^{14}N/^{15}N$ ratio.

Mass Spectrometry. The hydrochlorides of the rearrangement products were converted to ammonium sulfate by Kjeldahl digestion in the usual manner.[22] The ammonium sulfate solution was concentrated and oxidized with sodium hypobromite to nitrogen gas which was purified by the method of Ayrey et al.[15] The nitrogen isotope ratios were determined with a Wanless-Thode type double collection mass spectrometer.[25]

The kinetic isotope effects were calculated as described earlier.[15] The results are given in Table 1.

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(1) Part 13: J.-D. Cheng and H. J. Shine, *J. Org. Chem.*, **40**, 703 (1975).

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Control by Meta Substituents of Benzo–Vinyl Bonding Options during Triplet Sensitized Photorearrangement of Benzonorbornadienes and *anti*-7,8-Benzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-trienes

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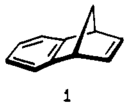
Abstract: A variety of meta-substituted benzonorbornadienes and *anti*-7,8-benzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-trienes were synthesized. Triplet sensitized photoisomerization of the benzonorbornadienes afforded one or both possible tetracyclo[5.4.0.0^{2,4}.0^{3,6}]undeca-1(7),8-10-trienes. For R = NO_2, $COOC_2H_5$, CN, and $COCH_3$, benzo-vinyl bridging to the para position of the aryl ring was followed exclusively. When the substituent groups were OCH_3, F, and NH_2, the di-π-methane rearrangement proceeded chiefly by meta aryl bonding (78, 91, and 70% respectively). This crossover in bonding preferences was also seen in the benzotricyclodecatriene series. In these latter systems, competitive [$_{\pi}2 + _{\pi}2$] intramolecular cycloaddition is also possible. When R = CN, only the di-π-methane rearrangement pathway is followed. In contrast, the methoxy derivative afforded 55% of the related benzobasketene and the *o,o'*-dimethoxy example gave rise to approximately 10% of bishomocubyl derivative. Accordingly, acceptor groups favor aryl-vinyl bonding while donor groups promote variable levels of [$_{\pi}2 + _{\pi}2$] bonding. It is concluded that this reactivity pattern is dictated by the nature and relative energy level of the higher singly occupied molecular orbital. The di-π-methane regioselectivity is shown not to be in harmony with the reactivity patterns expected from radical or electrophilic attack on the aromatic ring. Rather, the observed bridging regioselectivity is seen to conform to the substituent perturbations upon the electronic distributions of the triplet excited states, in full agreement with theoretical assessments of the question.

That benzenoid excited states differ from parent ground states both in electronic structure and reactivity is now a well-recognized fact.[1] During $\pi \rightarrow \pi^*$ excitation, an electron is promoted from one molecular orbital to a higher energy MO of the same π system. The resultant change in electron distribution is intimately related not only to the nature of the ring substituent(s), but also to the multiplicity of that excited state which is utilized. Although molecular orbital treatments of $S_{1\pi\pi}*$ excited states abound,[2] quantum mechanical descriptions of $T_{1\pi\pi}*$ electronic distributions, particularly as these are affected by electron-donating and -withdrawing groups, are almost entirely lacking.[3] Since the number of aromatic photochemical rearrangements which proceed via triplet states continues to grow, knowledge of substituent influences on the various bonding options gains considerable importance. Expectations that the elucidation of reactivity patterns would serve a predictive role in future experimental undertakings and act as an important link with theoretical calculations provided the impetus for the present study.

The striking features of the triplet-sensitized di-π-methane photoisomerizations of meta-substituted benzonorbornadiene (**1**) and *anti*-7,8-benzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (**2**)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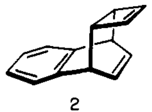
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