

The Mechanism of Photolytic Conversion of 2-Azidobiphenyl to Carbazole

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Abstract: The mechanism of conversion of 2-azidobiphenyl and substituted analogs to the corresponding carbazoles has been subjected to further study using flash photolysis and kinetic spectroscopy. The reaction is accompanied by an absorbance increase at 289 nm (carbazole formation) and an absorbance decrease at 360 nm (transient disappearance). In hexane, the two reactions occur at rates which are sufficiently different to indicate that two separate reactions are involved. For 2-azidobiphenyl-2',4',6'-d₃, there is no isotope effect for carbazole formation, but $k_H/k_D \approx 1.9$ for transient disappearance. The differences in rate constants for carbazole formation and transient disappearance are large in tetrahydrofuran and in methanol. Rate data for carbazole formation and transient decay in hexane, tetrahydrofuran, and acetonitrile for 2-azido-3',5'-dimethylbiphenyl are reported. The results closely parallel those of the parent compound. Corresponding data for 2-azido-3',5'-bis(trifluoromethyl)biphenyl were also obtained. These data are discussed and appear to require reinterpretation of previous mechanistic proposals which propose triplet 2-biphenylnitrene as the major carbazole precursor.

In terms of product yield, the photolytic conversion of 2-azidobiphenyl to carbazole is one of the cleanest reactions believed to proceed through an aryl nitrene intermediate.² This circumstance has prompted considerable mechanistic study of the reaction with the goal of defining the nature of the nitrene. The studies which are most pertinent to the results reported here are those in the laboratories of Reiser,³ Swenton,⁴ and Berry.⁵

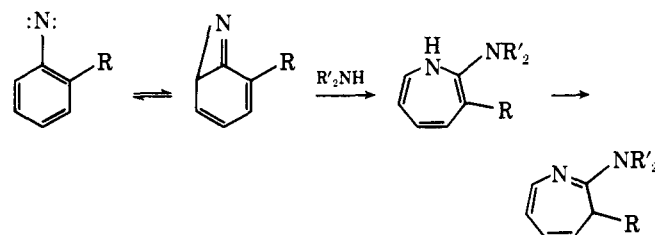
Reiser, Wagner, and Bowes^{3a} demonstrated that photolysis of 2-azidobiphenyl in a glass at 77 K led to an intermediate which had an absorbance maxima near 340 nm. This intermediate was shown on irradiation with light $\lambda > 320$ nm to be transformed to carbazole. The intermediate was assigned as triplet 2-biphenylnitrene on the basis of the similarity of its spectrum to that of other triplet aryl nitrenes.^{3b} The mechanism of the photochemical conversion of the intermediate to carbazole was regarded as uncertain. Subsequently Reiser and coworkers^{3c} examined the photolytic conversion of 2-azidobiphenyl to carbazole in a polymer matrix at room temperature. The disappearance of the absorbance at 340 nm was found to occur at a rate of about $1 \times 10^3 \text{ sec}^{-1}$. The reaction was implied to involve rate-determining intramolecular hydrogen abstraction, presumably followed by rapid collapse of the triplet diradical to give carbazole.

Swenton and coworkers⁴ studied quantum yields and product distribution as a function of solvent, quenchers, and sensitizers in solution at room temperature. It was assumed that direct excitation led to loss of nitrogen and formation of a nitrene which cyclized to carbazole, but no conclusion was reached about the multiplicity of the nitrene intermediate.

Lehman and Berry⁵ studied the conversion of 2-azidobiphenyl to carbazole by flash photolysis. They accurately established the rate of carbazole formation and the activation parameters of the reaction. They also roughly measured the rate of disappearance of an intermediate characterized by a spectrum closely similar to that described by Reiser, Wagner, and Bowes.^{3a} The agreement of the two rates (within a factor of 2 of one another) was taken as evidence that the two absorbance changes were associated with a single reaction. It was concluded that the reaction was the formation of carbazole from triplet 2-biphenylnitrene. The mechanism was further specified in that the rate-determining step was taken to be the addition of the nitrene to the π system

of the adjacent ring. A rapid hydrogen atom migration was proposed to complete the reaction. At 291.7°, they recorded a rate of 1110 sec^{-1} for carbazole formation.

We have been studying the reactions of aryl nitrenes both by flash photolysis and by trapping experiments.⁶ The Lehman-Berry mechanism does not account for the ability of nucleophilic traps (specifically secondary amines) to partially divert the nitrene toward ring expansion to an azepine.⁶ This rearrangement is a general reaction of aryl nitrenes^{6,7} and is usually rationalized in terms of a valence isomer of the singlet nitrene.²



The reaction rates of amines with the nitrene isomers are in the vicinity of 10^4 – $10^6 \text{ l. mol}^{-1} \text{ sec}^{-1}$ near room temperature.^{6a} If there were a single intermediate leading both to carbazole and azepine, it should therefore be very largely converted to azepine by an amine concentration of 1 M or less, but this is not the case.^{6b} Trapping is competitive with carbazole formation but not in a way compatible with a single intermediate. Instead it appears that there are two carbazole precursors, one which is competitively trapped by amines and one which is not.^{6b}

With the object of clarifying these points, we have measured the isotope effects of the reactions which follow photodecomposition of 2-azidobiphenyl-2',4',6'-d₃. We have also examined the effect of solvents and substituent groups on the rates of the reactions which occur following photolysis of 2-azidobiphenyls.

Results

Carbazole formation was followed by measuring the absorbance increase at 289 nm for all but the bis(trifluoromethyl) derivative which was monitored at 328 nm. First-order rates were measured for 2-azidobiphenyl (**1a**), 2-azido-3',5'-dimethylbiphenyl (**1b**), and 2-azido-3',5'-bis(trifluoromethyl)biphenyl (**1c**) in hexane, tetrahydrofuran, and

Table I

Compd	2,4,6 substituent	Solvent	Carbazole formation (289 nm) k , sec ⁻¹ ^a	Transient disappearance (λ 360 nm) k , sec ⁻¹ ^a
1a	H	Hexane	980	490
		Hexane	760	620
		(0.02 <i>M</i> piperylene)		
		Cyclohexane	960 ^b	
		Tetrahydrofuran	5.0×10^3	27
1a-d ₃	D	Acetonitrile	9.8×10^3	
		Methanol	19.6×10^3	9.9
		Cyclohexane	$1.0_2 \times 10^3$ ^b	260 ^b
		Tetrahydrofuran	4.9×10^3	11.3
1b	CH ₃	Hexane	1.3×10^3	390
		Hexane	1.1×10^3	410
		(0.02 <i>M</i> piperylene)		
		Tetrahydrofuran	6.7×10^3	12.4
		Acetonitrile	7.5×10^3	12.6
1c	CF ₃ ^c	Hexane	140	~140
		Hexane	96	~140
		(0.02 <i>M</i> piperylene)		
		Tetrahydrofuran	830	<i>d</i>
		Acetonitrile	1.6×10^3	<i>d</i>

^a Ambient temperature (20 ± 1°C) unless otherwise specified. ^b 18°C. ^c Carbazole formation monitored at >328 nm. ^d See text.

acetonitrile. The reaction was also studied in methanol in the case of **1a**. The unsubstituted compound **1a** was also studied in cyclohexane to permit direct comparison with the data of Lehman and Berry.⁵ At 291 K, we find $k = 960$ sec⁻¹ in satisfactory agreement with their value of 1110 at 291.7 K. The rate in hexane (980 sec⁻¹) was also within experimental error of the values in cyclohexane. The various rate constants for carbazole formation are reported in Table I.

To determine the kinetic isotope effect, 2-azidobiphenyl-2',4',6'-d₃ was synthesized. The rates of carbazole formation in cyclohexane and in THF are within experimental error of those observed for the undeuterated compound. The effect of added trifluoroacetic acid on the rate was examined for the unsubstituted 2-azidobiphenyl in THF. The concentration of added acid was varied from 1×10^{-3} to 0.27 *M* without effect on the rate of the absorbance change at 289 nm. The initial concentration of azide was varied over a fivefold range without effect on the rate of carbazole formation. The effect of added piperylene (10^{-2} *M*) in hexane was also examined. Carbazole formation rates decreased by 20–30%.

Also reported in Table I are measurements of rates of absorbance decrease at 360 nm. The absorbance change at this wavelength should measure disappearance of the intermediate previously observed by Reiser³ and by Lehman and Berry.⁵ The absorbance change at this wavelength is relatively small, and more concentrated solutions (5×10^{-5} to 1×10^{-4} *M*) were required than to measure carbazole formation ($\sim 6 \times 10^{-6}$ *M*). Reproducibility within ±10% was observed for the measured first-order rate constants for **1a**. The isotope effect was determined in hexane solution using deuterated **1a** and k_H/k_D was found to be 1.9. In THF, $k_H/k_D = 2.2$. In contrast to carbazole formation, the rate of transient disappearance decreased in the order hexane > tetrahydrofuran > methanol. Rates of transient disappearance were also measured for **1b** in hexane, tetrahydrofuran, and acetonitrile. The rate constant for transient disappearance is smaller than that for carbazole formation by a factor of >3 in hexane, and again the reactions show opposite responses to solvent polarity. In acetonitrile, carbazole formation is >600 times faster than transient disappearance.

In the case of the trifluoromethyl compound **1c**, the disappearance of the absorbance at 360 nm could not be ana-

lyzed as a simple first-order reaction in THF or acetonitrile. The absorbance–time plots were curved and appeared to be the sum of two first-order decays. However, the absence of initial concentrations (immediately after the flash) and extinction coefficients for the species involved precluded further analysis of the absorbance decay data.

The trifluoromethyl case was amenable to estimation of the rate of trapping of an intermediate by dibutylamine. Because of the experimental problems described below, the rate constant obtained for the trapping reaction is no better than ±50%. Specifically, the formation of azepine was monitored at 360 nm under conditions such that the contribution to the total absorbance from the “360 intermediate” was significant (20–40% of the total absorbance). Fortunately, on the time scale of the trapping reaction the absorbance of the “360 intermediate” does not decay significantly, and fairly reliable corrections could be made. The trapping reaction was studied using di-*n*-butylamine concentrations from 3.8×10^{-2} to 3.8×10^{-3} *M* in THF. The corrected absorbance increases were first-order under these conditions, and the k 's varied with the amine concentration as expected. The average (seven experiments) value of the second-order rate constant is $4.0 \pm 2.0 \times 10^5$ *M*⁻¹ sec⁻¹.

Finally, to be sure that photolysis of 2-azidobiphenyl in methanol was not complicated by attack of the weakly nucleophilic solvent on the intermediates, the steady illumination photolysis of the azide (5×10^{-5} *M*) at 253.7 nm was performed. The course of the photolysis was followed by uv spectrophotometry and indicated that >90% of the azide was converted to carbazole ($\epsilon_{292.5}$ (carbazole) $\approx 16,000$ *M*⁻¹ cm⁻¹ in CH₃OH). This is in line with Swenton's observation^{4c} that the solvent 2-propanol did not alter the product yields for photolysis of **1a** at $\lambda \geq 310$ nm.

Discussion

Where comparison is possible, our data are in agreement with that reported by Lehman and Berry.⁵ However, our new data on substituent effects and the effect of various solvents lead us to conclude that the mechanism of carbazole formation is more complex than suggested previously and that a triplet biphenylnitrene is not the principal intermediate leading to carbazole in our experiments.

The suggestion that the triplet nitrene is the major carbazole precursor is based on the assignment of Reiser et al.³ of the absorbance bands which appear in the near-ultraviolet when the appropriate azide is photolyzed in a matrix to the triplet nitrene and the observation of Lehman and Berry⁵ that the rate of decay of the solution “intermediate” observed at ~340–360 nm was within a factor of 2 of the grow-in rate of carbazole absorbance at 289 nm. Granting that Reiser's assignment of the triplet is correct and that the absorbance decay at 340–360 nm observed by Lehman and Berry in the case of 2-azidobiphenyl and by us for the unsubstituted and substituted azides in a variety of solvents is in part or completely due to triplet, the observed kinetics of the “360 intermediate” decay do not match the kinetics of carbazole formation. Although the rates of the two absorbance changes are within a factor of 2 in hexane, we consider the difference to be outside the error limits of our measurements. Further, only the 360-nm absorbance decrease shows an isotope effect, and this magnifies the rate difference between the two processes to a factor of 4. The data in THF reveal much larger differences. For carbazole formation, the rate constant is 5.0×10^3 sec⁻¹, but the rate constant for the absorbance decrease at 360 nm is about $\frac{1}{200}$ of this. This difference is magnified to nearly 2000 in methanol.

The exact nature and fate of the species responsible for the 360-nm absorption in our system is an interesting and

open question. Using the extinction coefficients of Reiser, Bowes, and Horne⁹ for 2-biphenylnitrene and our data, we calculate that up to 18% of the photolyzed azide could yield triplet nitrene if all the absorbance at 360 nm is due to this species. If the triplet then reacts to form *trans*-azo-2-biphenyl, we should see a sizable increase in absorption at 360 nm since $\epsilon(\text{azo}) > 10\epsilon(\text{nitrene})$. That this is not the case in our air-saturated solutions is consistent with the report of Swenton et al.^{4c} that oxygen saturation completely suppressed azo compound formation in the direct photolysis of a 2-azidobiphenyl in benzene. It is possible that the nitrene reacts with the dissolved oxygen ($\sim 10^{-4} M$) in what would be a pseudo-first-order reaction under our conditions. A similar reaction was observed by Brinen and Singh¹⁰ at 77 K in the photolysis of a series of aryl azides. The final product of such a reaction could reasonably be a nitro compound and thus is not expected to have a strong absorption at the monitoring wavelength. It should be noted that, in the recent study of Lehman and Berry,⁵ the solutions used were degassed and the species responsible for the 360-nm absorbance may have a different fate than in our system.

We might also inquire as to whether the absorbance at 360 nm might be due to two species, one weakly absorbing (the triplet nitrene) and leading to carbazole, the other strongly absorbing and not leading to carbazole formation. The observed absorbances at λ 360 nm for 2-azidobiphenyl photolysis in THF were on the order of $0.01 \leq A \leq 0.025$. The extent of azide photolysis was typically 50–60% of the $2-4 \times 10^{-5} M$ solutions. If even 10% of the carbazole formed came from the triplet, we would have detected its rapid decay at 360 nm as it would have produced a readily detectable change in the absorbance at that wavelength, $\epsilon(2\text{-biphenylnitrene}) \approx 1000 M^{-1} \text{ cm}^{-1}$ at λ 360 nm, $l = 5$ cm.

These data permit the conclusion that, in hexane, carbazole formation does not take place exclusively from the transient which absorbs at 360 nm.⁸ For THF and methanol, a stronger statement can be made. No significant amount of carbazole is formed in the reaction accompanied by absorbance decrease at 360 nm. This reaction is sufficiently slow that a two-stage carbazole formation should be observed if disappearance of the transient was accompanied by carbazole formation. The oscilloscope photographs show no increase in absorbance at 289 nm during the time in which the absorbance at 360 nm decreases. We conclude that, irrespective of the identity of the absorbing transient, it is not the *only* carbazole precursor in hexane nor a *major* carbazole precursor in THF or methanol.

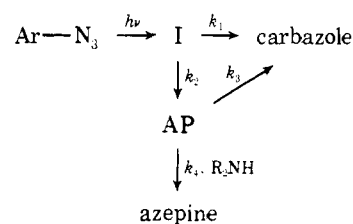
Examination of Table I shows that similar arguments and conclusions apply to 3',5'-dimethyl-2-azidobiphenyl.

The amine trapping reaction can provide further data on the mechanism. Sundberg and Heintzelman^{6b} have shown that each of the azides studied here gives rise to some azepine, as well as carbazole, when the photolysis is carried out in the presence of secondary amines. We have previously reported kinetic data on the azepine-forming process with phenyl azide and substituted phenyl azides which show that azepines are formed as a result of trapping of an intermediate generated by azide photolysis.^{6a} That is, the amines do not react with a photoexcited azide molecule. For **1a** and **1b**, significant amounts of azepines are formed only at concentrations of amine greater than 0.5 *M* and this circumstance precludes measurement of azepine formation rates for these compounds with our present equipment. For **1c**, azepine formation is significant even with 0.05 *M* amine, and the rate of azepine formation falls in an experimentally accessible range. The measured rate constant (22°C) for the reaction of the intermediate generated from **1c** with di-*n*-butylamine in THF is $\sim 4.0 \pm 2.0 \times 10^5 M^{-1} \text{ sec}^{-1}$. For-

mation of the substituted carbazole under the same conditions occurs with $k = 830 \text{ sec}^{-1}$. Thus 0.1 *M* amine should be sufficient to trap $\sim 98\%$ of the intermediate if there were a single intermediate but, in fact, $\sim 20\%$ of the azide appears as carbazole. Indeed, amine concentrations up to 0.5 *M* do not reduce the carbazole yield below 15%. This result strongly suggests, as proposed earlier,^{6b} that there are two carbazole precursors generated from **1c** and that only one can be diverted to azepine in the presence of an amine trap. The behavior of **1a** and **1b** is qualitatively suggestive of the same conclusion.^{6b}

There are at least two minimal mechanisms which can account for the available data. All the 2-azidobiphenyl may be converted to an intermediate I which is partitioned between carbazole and azepine precursor AP very rapidly (see Mechanism 1). If this mechanism is operative, it is the process governed by k_3 which is measured in our experiments, and *some carbazole is formed at a much faster rate*. This latter corresponds to the nontrappable fraction of carbazole.

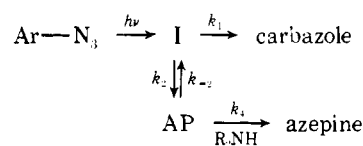
Mechanism 1



where $k_1, k_2 \gg k_3, k_4$

Alternatively, I and AP might be interconvertible (see Mechanism 2). In this mechanism, k_{-2} would be the rate constant governing the observed rate of carbazole formation with the observed rate constant $k_{\text{obsd}} = k_{-2}[k_1/(k_1 + k_2)]$. Again, some carbazole would be formed in a much faster process.

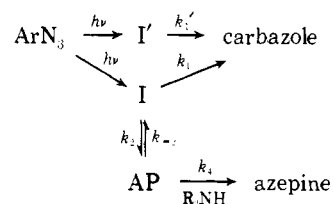
Mechanism 2



where $k_1 \approx k_2 > k_{-2}$

Finally, we note that the data can be fitted to a mechanism involving two intermediates formed on photolysis of the azide such as shown in Mechanism 3. That portion of the azide converted to I' would be nontrappable and would be converted to carbazole at a rate too fast to measure under our conditions. The observed rate of carbazole formation would be a function of k_1 , k_2 , and k_{-2} .

Mechanism 3



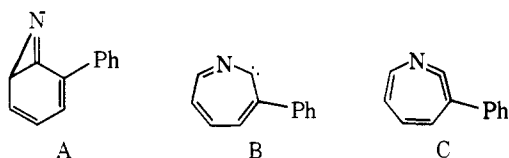
where $k_1' > k_1$

Besides the existence of a pathway to carbazole which is not subject to diversion by secondary amines, there is per-

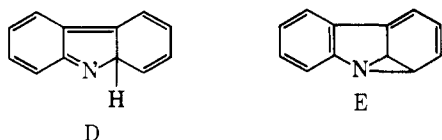
haps a qualitative indication that some carbazole is formed very rapidly in the reported spectrum at 50 μ sec after photolysis.⁵ Peaks interpreted as belonging to carbazole are present. Assuming the temperature of these measurements was near 295 K, the carbazole formation process with $k \approx 1.5 \times 10^3 \text{ sec}^{-1}$ would be less than 10% complete. Thus the appearance of distinct features attributable to carbazole as early as 50 μ sec is suggestive of an independent, very rapid, carbazole-forming process. Unfortunately, the absence of an accurate spectrum of the transient at room temperature in solution frustrates any attempt to estimate the amount of carbazole indicated by the 50 μ sec spectrum.

The present data do not allow a clear choice among the various mechanisms. They do, however, exclude mechanisms in which only one intermediate can lead to carbazole. The weight of the evidence is that, under our conditions, the absorbance change at 360 nm and that at 289–320 nm are the result of two different processes. The rate constants differ significantly, only the former reaction shows an isotope effect, and the two reactions show opposite responses to changes in the polarity of the solvent. The transient which was observed by Lehman and Berry and whose decay we have followed could be triplet 2-biphenylnitrene provided that (a) it is a minor component of the over-all system so that the amount of carbazole formed via triplet nitrene is negligible or (b) it does not lead to carbazole. The absorbance changes associated with the decay of this transient are small relative to the change associated with carbazole formation. This is expected since the monitoring wavelength is on the tail of the reported transient peak. Nevertheless, the fact that in THF and methanol there is no carbazole formation occurring at a rate corresponding to the disappearance of the "360 nm transient" clearly indicates that this transient is not a significant carbazole precursor.

The data in the present study provide no direct evidence about the structures of the intermediates. Previous work on aryl azides provides some basis for suggesting structures, however. The structure normally associated with the azepine precursor (AP) is the azirine (A). Conceivable alternatives are an azabicycloheptatrienyldiene (B) or a cyclic ketenimine (C). Singlet biphenylnitrene could be I in each



of the mechanisms. Alternative carbazole precursors are D and E. Intermediate D could be formed by electrophilic attack of singlet nitrene on the adjacent ring,¹¹ whereas E is



an addition intermediate of the type formed when many carbenes react with aromatic rings.¹² We do not believe either is likely to be the long-lived intermediate whose transformation to carbazole is followed (289–320 nm) under the present conditions. D should be detectable by the disappearance of long wavelength absorbance. Both D and E would

appear to be susceptible to acid-catalyzed conversion to carbazole yet acid is without effect on the observed rate of formation. These observations do not exclude D or E from being I' in Mechanism 3 since this process would not be observed in our measurements.

Clearly, the system has not yielded all its secrets. However, our data appear to require reinterpretation of the previous proposal in which triplet 2-biphenylnitrene is the sole or major carbazole precursor.

Experimental Section

Materials. The azides **1a**, **1b**, and **1c** were prepared by Heintzelman in the course of a related study.^{6b} The deuterated **1a** was prepared from aniline- d_3 obtained by the method of Langenbucher, Mecke, and Schmid.¹³ This was converted in sequence to iodobenzene-2,4,6- d_3 (HONO, then KI), 2-nitrophenyl-2',4',6'- d_3 (Ullmann coupling with 2-bromonitrobenzene), 2-aminobiphenyl-2',4',6'- d_3 (catalytic reduction), and 2-azidobiphenyl-2',4',6'- d_3 (HONO, then NaN_3). The extent of labeling was determined from the molecular ion at 15 eV to be 95% d_3 , 5% d_2 , and <1% d_1 .

The hexane was distilled from Na–Pb and tetrahydrofuran was distilled from lithium aluminum hydride. Cyclohexane was stirred over night with an equal volume of sulfuric acid, washed with water and 10% sodium hydroxide, and dried over sodium hydroxide pellets. It was then distilled from Pb–Na.

Apparatus and Procedures. The flash apparatus was of standard design and has been described elsewhere.^{6a,14} Absorbance data were obtained from Polaroid photographs of the oscilloscope traces. First-order rate constants were obtained from least-squares plots.

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References and Notes

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