proton has a considerable rotational freedom around the two cylindrically symmetric π orbitals in the ground state. With arylacetylenes **9** and **10** the ν_{OH} band showed two bonded OH peaks, the α and β bands. By comparing with the frequency shifts and the thermodynamic data of alkylbenzenes[3-5,28b] and olefins,[6,15] the α and β bands seem to be due to hydrogen bonding with the aromatic π electron delocalized through the whole molecule like that of styrene and stilbene and with the double bond perpendicular to the aromatic ring, respectively. West[7] attributed the β band to the hydrogen bonding of the triple bond; our considertions, however, seem to be more reasonable since the thermodynamic values of our complexes (β band) are closer to the values of olefins than those of aliphatic acetylenes.[38] As shown in Table I, $\Delta S°$ for complex formation with alkylallenes are smaller than those for alkylacetylenes and are larger than those for olefins. This could be explained by the rotational model of the phenolic proton around the two circular p orbitals of the central sp carbon as the hydrogen bonding configuration for alkylallenes. Arylallenes **17–19** did not show splitting of the bonded ν_{OH} spectra and the frequency shifts and thermodynamic results are nearly identical with those of styrene and α-methylstyrene.[15] In arylallenes $-\Delta F$ *vs.* $\Delta\nu$ plots lie near the line obtained for phenol–alkylbenzene complexes. Such was the case for the phenol–phenylcyclopropane complex.[39] This suggests that the hydrogen bonding is to the benzene ring rather than to the terminal ethylenic linkage.[40,41] This consideration is supported from the entropy anomaly[3,4] observed for the complex involving arylallenes: $-\Delta S$ for their complex formation are smaller than the values observed for alkylallenes and olefins; their magnitudes are nearly equal to those for aryl olefins (styrene and α-methylstyrene[15]). From these results we believe that arylallenes act as monofunctional π bases, suggesting a configuration with the phenolic proton lying over the 6π-electron system of styrene and not near the terminal ethylenic fragment.

Acknowledgment. We wish to thank Professor P. v. R. Schleyer of Princeton University for valuable discussions and Mr. F. Takabayashi for taking some infrared spectra.

(38) As pointed out by a referee, the α and β bands can be attributed to hydrogen bonding with the phenyl ring and with the triple bond, respectively. Although this interpretation cannot be ruled out from our present data, we believe that our model explains more reasonably the $-\Delta F$ *vs.* $\Delta\nu$ plots in the α and β bands for arylacetylenes (Figure 4).

(39) Z. Yoshida, N. Ishibe, and H. Kusumoto, *J. Amer. Chem. Soc.*, **91**, 2279 (1969).

(40) The possibility of interaction with the central sp-hybridized carbon of arylallene cannot be excluded.[35] However, if that were the case, $-\Delta F$ *vs.* $\Delta\nu$ plots in arylallenes would lie in a similar region to those in alkylallenes.

(41) For 1,1-diphenylallene (**19**), correction of the equilibrium constant by the statistical factor, 2, gave the ΔF value -0.62 kcal/mol. The plot of this value *vs.* $\Delta\nu$ lies more closely to the line obtained for phenol–alkylbenzene complexes.

Cyclization of 2-Azidobenzophenones to 3-Phenylanthranils. An Example of an Intramolecular 1,3-Dipolar Addition[1]

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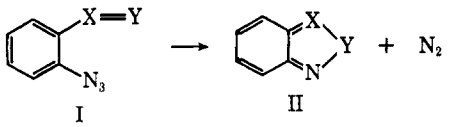
Received June 14, 1971

Abstract: The rate of decomposition of 4′-substituted-2-azidobenzophenones to give 4′-substituted-3-phenylanthranils has been studied in decalin over a 45° temperature range. The reaction was found to be accelerated by electron-withdrawing groups and retarded by electron-donating groups. The enthalpy of activation was found to be considerably less than reported for phenyl azide decompositions. The entropy of activation was moderately large and negative (-6 to -21 cal deg^{-1} mol^{-1}). A plot of $\Delta H^{\ddagger}$ *vs.* $\Delta S^{\ddagger}$ was linear. An isokinetic temperature of 163° was calculated. The reaction was accelerated only slightly in changing the solvent from decalin to anisole to dimethylformamide. A 1,3-dipolar addition mechanism is proposed to account for these results.

Ortho-substituted phenyl azides have often been found to decompose much more rapidly than the corresponding meta or para isomers. This rate enhancement has been noted primarily in those systems where the ortho substituent has some type of α,β-unsaturation and in which the decomposition leads to



I II

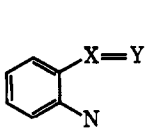
cyclization. Several workers[3] have suggested that the reaction does not involve a nitrene intermediate (III), but instead proceeds *via* a concerted mechanism (IV) in which cyclization and loss of nitrogen are concurrent.

The evidence against the involvement of a nitrene is (a) the nitrene intermediate cannot account for the rate

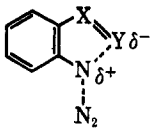
(1) This work was supported in part by the Petroleum Research Fund administered by the American Chemical Society. This material was presented in part at the 2nd International Congress of Heterocyclic Chemistry, Montpellier, France, July, 1969.

(2) (a) Abstracted in part from the M.S. Thesis of F. E. Behr, Southern Illinois University, June, 1968, and from the M.S. Thesis of R. L. Reed, Southern Illinois University, Sept, 1969; (b) American Chemical Society Fellow, summer, 1969.

(3) See L. K. Dyall and J. E. Kemp, *J. Chem. Soc. B*, 976 (1968), and references therein.



III



IV

enhancement and (b) those products normally associated with arylnitrene formation, *i.e.*, insertion products, azo compounds, anilines, and polymers, have not generally been observed. In fact, the reactions are known for their lack of significant amounts of by-products.

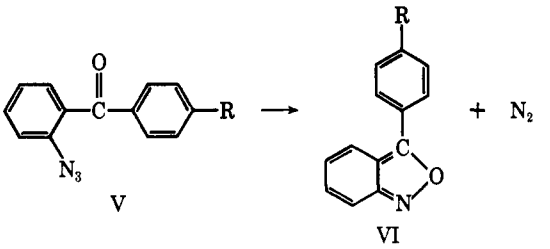
Some time ago we began to suspect that the explanation of the rate enhancement on the basis of neighboring group participation was oversimplified. The first indication of this was the observation that in the decomposition of *o*-azidobiphenyls to give carbazoles, the rate of nitrogen loss was enhanced by the *o*-phenyl group only by a factor of about 2 at 163°.[4] Further, the effect of substituents para to the azido group was found to be essentially the same in *o*-azidobiphenyls as in simple phenyl azides; both electron-donating and electron-withdrawing substituents enhanced the rate of nitrogen evolution. These results suggested that the phenyl ring was not capable of participating as a neighboring group.

The second indication that the neighboring group idea may not be correct was the qualitative observation that the decomposition temperatures of anils of *o*-azidobenzaldehyde were not significantly different from the decomposition temperatures of anils derived from *o*-azidoaniline,[5] in spite of the fact that in the former case cyclization is to the more nucleophilic nitrogen, while in the latter case cyclization is to carbon.

Further, we have observed several cases where *o*-azidoazobenzenes decompose to give benzotriazoles at temperatures below 50°.[3,6] The nitrogen atoms of azobenzene are not known for their nucleophilicity, and yet, the greatest rate enhancement is observed in this system.

In order to obtain more quantitative information on the rate enhancement and to obtain some knowledge about the electronic nature of the transition state in these reactions, a series of kinetic studies was undertaken. The only two systems that have had a systematic kinetic study are the cyclization of *o*-azidobiphenyls to give carbazoles[4] and the cyclization of *o*-azidonitrobenzenes to give furoxans.[3,7]

As our initial system for study, we chose the cyclization of *o*-azidobenzophenones to give anthranils.[8] It was reasoned that if the reaction was concerted, the nitrogen to which the cyclization occurred should be "nitrene like" and therefore electron deficient. Further it was reasoned that by placing substituents in the 4′ position, the electron density on the carbonyl oxygen could be varied and that this in turn would vary the



V VI

concertedness of the reaction. On the basis of these assumptions, one would predict that the rate of nitrogen evolution should be accelerated by electron-donating groups and retarded by electron-withdrawing groups.

The desired *o*-azidobenzophenones were all prepared by diazotization of the corresponding *o*-aminobenzophenone, followed by treatment of the diazonium salt with sodium azide. Their properties are listed in Table I.[9] With the exception of 2-amino-4′-nitrobenzophenone, the 2-amino-4′-substituted benzophenones were prepared by modifications of the method reported by DeTar and coworkers.[10]

Table I. Physical Properties of 2-Azido-4′-R-benzophenones and 3-(4-R-Phenyl)anthranils

R	Mp, °C	Yield, %[a]
	2-Azido-4′-R-benzophenones[c]	
H	*b*	
CH_3	77.5–76.0	98
Br	62.5–63.5	68
CH_3O	73.5–74.5	85
NO_2	110–111	67
Cl	48–49	85
$CH(CH_3)_2$	72.5–73.0	53
$C(CH_3)_3$	90–91	55
	3-(4-R-Phenyl)anthranils[c]	
H	51.5–52.5[d]	39[e]
CH_3	92–92.5[f]	73
Br	149.5–150.5[g]	70
CH_3O	99.0–99.5	73
NO_2	252–254[i]	97 (80)[h]
Cl	153.5–154.5[j]	73
$CH(CH_3)_2$	74.5–75.5	98
$C(CH_3)_3$	153.0–153.5	85

[a] Isolated yields. [b] Never crystallized. See ref 8. It was purified on an alumina column by elution with 1:1 petroleum ether:benzene. [c] All solids were purified by recrystallization from ethanol or aqueous ethanol except where noted. [d] Reported 53°, ref 8. [e] The low isolated yield was due to extreme solubility in all common solvents. See ref 8. [f] Reported 95.5°, see A. Kliegl, *Chem. Ber.*, **41**, 1848 (1908). [g] Reported 155°, see N. Campbell and H. F. Andrew, *Proc. Roy. Soc. Edinburgh, Sect. A*, **66** (4), 252 (1963–1964). [h] Oxidation of the benzamide with NaOBr. See Experimental Section. [i] Recrystallized from aqueous DMF. [j] Reported 152°, see I. Tanasescu and A. Silberg, *Bull. Soc. Chim. Fr.*, [5] **3**, 2383 (1936).

The synthetic sequence used to prepare 2-amino-4′-nitrobenzophenone involved the low-temperature inverse addition of *p*-tolylmagnesium bromide to *p*-nitrobenzaldehyde to give 2-methyl-4′-nitrobenzhydrol.

(4) P. A. S. Smith and J. H. Hall, *J. Amer. Chem. Soc.*, **84**, 480 (1962).
(5) Compare (a) L. Krbechek and H. Takimoto, *J. Org. Chem.*, **29**, 1150 (1964); (b) *ibid.*, **29**, 3630 (1964); (c) J. H. Hall and D. R. Kamm, *ibid.*, **30**, 2092 (1965).
(6) (a) J. H. Hall and F. W. Dolan, unpublished results; (b) J. H. Hall, *J. Org. Chem.*, **33**, 2954 (1968).
(7) (a) T. F. Fagley, J. R. Sutter, and R. L. Oglukian, *J. Amer. Chem. Soc.*, **78**, 5567 (1956); (b) E. A. Birkhimer, B. Norup, and T. A. Bak, *Acta Chem. Scand.*, **14**, 1894 (1960); (c) *ibid.*, **14**, 1899 (1960).
(8) P. A. S. Smith, B. B. Brown, R. K. Putney, and R. F. Reinisch, *J. Amer. Chem. Soc.*, **75**, 6335 (1953).
(9) The analytical properties (Table Ib) for these compounds will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-4952. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.
(10) H. J. Scheifele, Jr., and D. F. DeTar, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 34.

Table II. Rates of Decomposition of 2-Azido-4′-R-benzophenones in Decalin[a,b]

Temp, °C	$k \times 10^2$, min^{-1} 4′-OCH_3	4′-CH_3	H	4′-Br	4′-NO_2
105.0	0.416[c]	0.471 ± 0.008	0.581 ± 0.07	0.723 ± 0.03	
120.0	1.36 ± 0.04	1.96 ± 0.09	2.14[c]	2.16 ± 0.01	3.42[c]
127.0					5.24[c]
135.0	5.00 ± 0.05	7.06 ± 0.01	7.05 ± 0.20	7.36 ± 0.02	8.90[c]

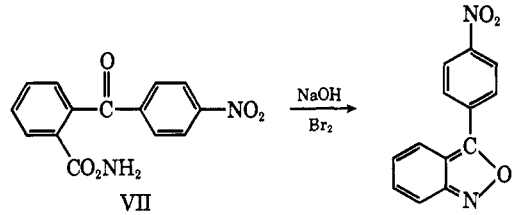
[a] See footnote 11. [b] Errors are average deviations. [c] Single determinations.

Table III. Rates of Decomposition of 2-Azido-4-R-benzophenones[a-c]

Temp, °C	$k \times 10^2$, min^{-1} 4′-$C(CH_3)_3$	4′-$CH(CH_3)_2$	4′-CH_3	4′-Cl	4′-Br
104.98	0.469 ± 0.05				
104.87		0.607 ± 0.02		0.650 ± 0.10	
119.80		1.88 ± 0.02			
119.90	1.79 ± 0.05		1.64 ± 0.13		
119.95				1.93 ± 0.04	
134.92		9.06 ± 0.03[d]			
134.95					7.85 ± 0.05
134.97	7.59 ± 0.01				
135.00		7.53 ± 0.14		7.70 ± 0.05	
135.05		8.91 ± 0.04[e]			
150.00		22.0 ± 0.1			
160.40		38.2 ± 0.2			
160.44	41.3 ± 0.9				
160.47				44.0 ± 0.1	

[a] See footnote 11. [b] Errors are average deviations. [c] The solvent was decalin except where noted. [d] In dimethylformamide. [e] In anisole.

Oxidation of this compound with chromium trioxide–phosphoric acid gave a mixture of 2-methyl-4′-nitrobenzophenone and 2-carboxy-4′-nitrobenzophenone. Conversion of the latter compound to the amino ketone was accomplished *via* the acyl chloride, acyl azide, isocyanate, amine route. Attempts to prepare the amine by oxidation of the corresponding amide with bromine in aqueous base gave instead an 80% yield of 3-(4-nitrophenyl)anthranil.



VII VIII

The rate of decomposition of each of the 4′-substituted-2-azidobenzophenones was determined by following the rate of nitrogen evolution. Decalin was used as the solvent except where noted. The calculated first-order rate constants are listed in Table II and Table III.[11]

As can be seen in these tables, the change in the rate of decomposition with substituent is not very large. Comparison of the rate constants at 105 and 120° in Table II reveals that the reaction is accelerated by electron-withdrawing groups and retarded by electron-donating groups. The reaction rate is not greatly affected by solvent, but as shown in Table III, the rate of decomposition of 4′-isopropyl-2-azidobenzophenone was accelerated by about 20% in going from decalin to anisole to dimethylformamide.

(11) The data reported here are the result of two independent studies by F. Behr (Table II) and R. Reed (Table III).

The enthalpy and entropy of activation for each of the azides are listed in Table IV. The enthalpy of activation varies from 20.5 to 27 kcal mol^{-1}. The entropy of activation is in all cases negative, varying from −21.4 to −6.7 cal deg^{-1} mol^{-1}. The entropy of activation is a linear function of the enthalpy of activation as shown in Figure 1. From the slope of the plot, an isokinetic region of approximately 163 ± 10° was calculated. As can be seen in Tables II and III, at 135° the magnitude of the substituent effect is much smaller than at 105°. In Table III, at 160°, it is seen that the substituent effect has essentially disappeared. In fact the rate of decomposition of 4′-(*tert*-butyl)-2-azidobenzophenone is slower than the 4′-isopropyl derivative at lower temperatures, but at 160°, the *tert*-butyl derivative is actually faster. This appears to be one of the very few examples of a reaction where the rate has been determined on both sides of an isokinetic point. Unfortunately the reaction is too fast above 160° to extend the measurements beyond this point.

Table IV. Activation Parameters for 4′-R-2-Azidobenzophenones

R	$\Delta S^{\ddagger}$,[a] cal deg^{-1} mol^{-1}	$\Delta H^{\ddagger}$,[a] kcal mol^{-1}
OCH_3	−11.7 ± 1.5	26.0 ± 0.6
$C(CH_3)_3$	−9.7 ± 2.5	25.7 ± 1.0
$CH(CH_3)_2$	−14.3 ± 2.0	23.8 ± 0.8
CH_3	−6.7 ± 3.2	26.9 ± 1.3
H	−11.5 ± 0.3	24.8 ± 0.1
Cl	−13.1 ± 1.5	24.2 ± 0.6
Br	−14.9 ± 3.0	23.5 ± 1.2
NO_2	−21.4 ± 1.3	20.5 ± 0.5

[a] The errors given were estimated from the extreme slopes of a log k/T *vs.* $1/T$ plot.

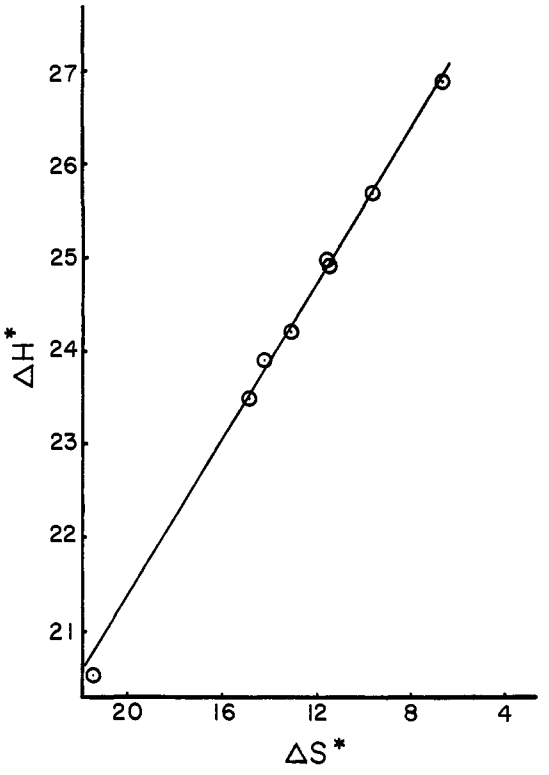


Figure 1. $\Delta H^{\ddagger}$ *vs.* $\Delta S^{\ddagger}$.

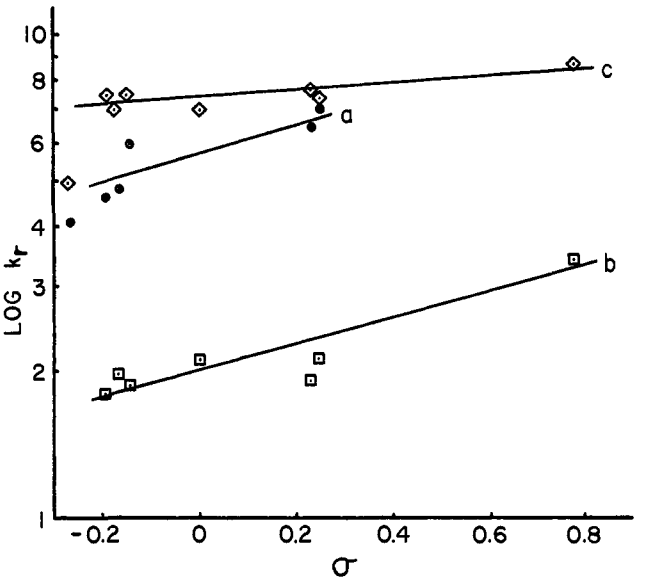


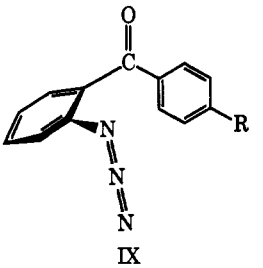
Figure 2. Hammett σ *vs.* log k_r: (a) 105°, log $k_r \times 10^3$; (b) 120°, log $k_r \times 10^2$; (c) 135°, log $k_r \times 10^2$.

In Figure 2 is shown the Hammett plot of the kinetic data at each of three temperatures. In each case the *p*-methoxy group fell below the line. A least-squares fit of the data, exclusive of the *p*-methoxy group, gave ρ values of 0.377, 0.293, and 0.140 at 105, 120 and 135°, respectively.

Discussion

The rate constants listed in Tables II and III for *o*-azidobenzophenones are approximately 40 times greater than the rate constants reported for meta- and para-substituted phenyl azides[4,12] and about 20 times greater than that reported for 4- and 5-substituted-2-azidobiphenyls.[2] Further, in meta- and para-substituted phenyl azides, as well as in the 2-azidobiphenyls, all substituents increased the rate of decomposition, there being no correlation with the Hammett equation.[4] Both the enhanced rate and the different substituent effect observed with the 2-azidobenzophenones indicate that they do not go through nitrene intermediates. Also the substituent effects observed here cannot be due primarily to the effect of the substituent directly on the azido group. Indeed the most favorable conformation for the 2-azidobenzophenones would be with the azide bearing ring twisted out of conjugation with the carbonyl group and the substituent bearing ring; thus the principal effect of the substituent should be on the carbonyl oxygen, not on the azido group.

If it is assumed that the decomposition is concerted, *i.e.*, nitrogen loss and N–O bond formation are synchronous, then the transition state should be best described as nucleophilic attack of oxygen on a nitrene-like, electron-deficient nitrogen. In this type of transition state, the substituent bearing ring would also be bent out of the plane due to the *o*,*o*′-hydrogen–hydrogen interaction and therefore the principal effect of the substituent should be on the carbonyl oxygen. On the basis of this picture one would predict that electron-donating groups, which increase the electron density on the carbonyl oxygen, would be expected to enhance the rate, while electron-withdrawing groups should retard the rate. This is just the opposite of what is observed.



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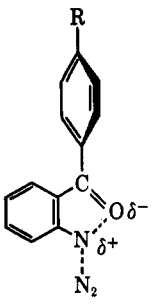
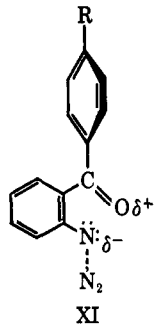


X

If this picture of the transition state is incorrect, what are the alternatives? One possibility would be to reverse the polarity of the reaction and describe it as nucleophilic attack of the azido nitrogen (N-1) on the carbonyl oxygen. However, the idea of a nucleophilic attack of nitrogen on the more electronegative carbonyl oxygen is without precedent and we are rejecting this idea on the basis of mechanistic improbability.

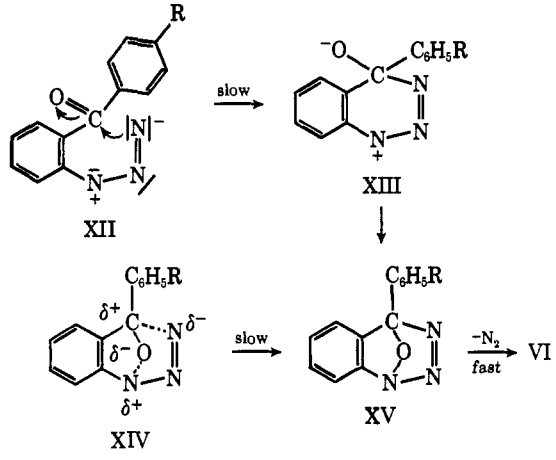
A much better explanation for the data involves a slow, rate-determining, nucleophilic attack of the terminal azide nitrogen (N-3) on the carbonyl carbon to

(12) M. Appl and R. Huisgen, *Chem. Ber.*, **92**, 2961 (1959).



XI

give the bicyclic intermediate XV, followed by a rapid loss of nitrogen. The formation of XV could be



XII XIII XIV XV VI

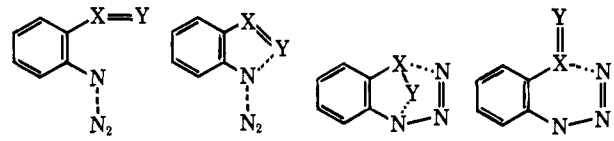
visualized as being formed in a stepwise fashion, involving a zwitterion XIII, or it could be visualized as an intramolecular 1,3-dipolar addition as shown in XIV. Either XII or XIV could explain the acceleration of the rate by electron-withdrawing groups and retardation by electron-donating groups; however, in the latter case, one must assume that C–N bond formation is slightly ahead of C–O bond formation. If the reaction were to take place stepwise with the formation of the zwitterion XIII, one would anticipate that the reaction would be accelerated by more ionizing solvents. However, the decomposition of 4′-isopropyl-2-azidobenzophenone in dimethylformamide increased the rate only by a factor of 20% over that in decalin. This suggests a rather nonpolar transition state.

Both the small substituent effect and the small solvent effect are quite consistent with the 1,3-dipolar transition state XIV. Indeed these are characteristics of intermolecular 1,3-dipolar additions.[13] Another characteristic of intermolecular 1,3-dipolar additions is the very large negative entropy of activation. For example, in the addition of phenyl azide to olefins, values of -30 to -35 cal deg^{-1} mol^{-1} have been reported.[14] The values obtained here are negative, but as can be seen in Table IV, not nearly as negative as in the intermolecular process. However, the difference of 15 to 20 cal deg^{-1} mol^{-1} is about the normal difference expected between an intermolecular and an intramolecular process. Thus the values in Table IV are consistent with an intramolecular 1,3-dipolar transition state.

One objection that could be raised to the 1,3-dipolar transition state is that it requires a bent azido group. However, molecular orbital calculations have indicated that the energy difference between linear and bent forms of the azido group is small.[15]

If the decomposition of 2-azidobenzophenones is an intramolecular 1,3-dipolar addition, then the question as to whether an azide can be added intermolecularly to benzophenone should be asked. In order to check this point, the rate of decomposition of phenyl azide in decalin in the absence and in the presence of a several mole excess of benzophenone was determined. The added benzophenone had no effect on the rate of nitrogen evolution. This negative result can be rationalized on the basis that the entropy of activation must be too negative to allow the intermolecular addition to take place at a temperature below the decomposition temperature of phenyl azide.

The mechanisms considered here for azide cyclization may not be discrete reaction paths, but in reality may represent a spectrum of paths. Examining the transition states pictured (XVI–XIX), it can be seen

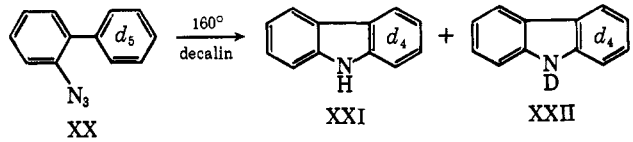


XVI XVII XVIII XIX

that there is a continuous spectrum of transition states possible, varying in the relative degrees of N-1 to Y *vs.* N-3 to X bond formation. Which of these extremes is of lowest energy should depend only on the nature of X and Y. Thus there is no reason to believe that the decomposition of azides with α,β-unsaturation should all occur by the same mechanism.

To illustrate this further, the information published by Dyall and Kemp[3] suggests that *o*-nitrophenyl azides decompose by a path best represented by XVII. Although evaluation of the substituent effects in this system is difficult, since the substituent affects both the azido group and the nitro group, the evidence presented by these workers based on steric factors seems to be on solid ground. In fact the 1,3-dipolar transition state postulated here for 2-azidobenzophenones does not seem too likely in the *o*-azidonitrobenzenes, since nitro groups on aromatic rings are not normally subject to attack by nucleophiles.

The 2-azidobiphenyl system is the prime example of a system in which the transition state XVI is involved. Perhaps the best evidence for the involvement of the nitrene is the following experiment performed in this laboratory several years ago. 2-Azidobiphenyl, in which the ring to which the cyclization occurs was completely deuterated, was decomposed in decalin and the resulting carbazole isolated. It was found by infrared to contain about 67% N–D bonds and 33% N–H bonds. This experiment clearly indicates that a nitrene is formed, which can either abstract hydrogen from the



XX XXI XXII

(13) R. Huisgen, *Proc. Chem. Soc.*, 1632 (1962).
(14) P. Sheiner, J. H. Schomaker, S. Deming, W. J. Libbey, and G. P. Nowack, *J. Amer. Chem. Soc.*, 87, 306 (1965).
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solvent or deuterium from the aromatic ring, prior to cyclization.

Experimental Section

2-Amino-4′-substituted-benzophenones. Except for 4′-nitro- and 4′-methoxy-2-aminobenzophenones, a modification of the DeTar[10] procedure was used. The following general procedure was found to give moderate to poor yields of the amino ketones. A mixture of 36.5 g (0.125 mol) of *N*-toluenesulfonylanthranilic acid,[10] 190 ml of dry chlorobenzene (or other appropriately substituted benzene derivative), and 29.7 g (0.143 mol) of phosphorus pentachloride was heated at 50° for 30 min. The dark solution was cooled to room temperature and 72.5 g (0.44 mol) of anhydrous aluminum chloride was added in four portions. The reaction was heated at 85–90° for 10 hr. With electron-donating substituents, such as *tert*-butyl and isopropyl, 5 hr at 85–90° was used and with methyl, 4 hr at 75° was sufficient. The mixture was cooled and poured over 125 g of ice and 10 ml of 12 *N* hydrochloric acid was added. Excess solvent was removed under vacuum. Excessive heat during the distillation must be avoided to prevent the mass from melting and becoming unfilterable. The solid was filtered and washed with warm 6 *N* hydrochloric acid, water, 5% potassium carbonate, and then water again. The crude sulfonamide was placed in 400 ml of concentrated sulfuric acid and the solution heated on a steam bath for 1 hr. The reaction mixture was cooled in an ice bath and diluted by the addition of 400 g of ice. The insoluble product, *p*-chlorophenyl *p*-tolyl sulfone, was filtered and discarded. The filtrate was decolorized with charcoal. The sulfuric acid solution was cooled in an ice bath and neutralized with concentrated ammonium hydroxide (1200 ml). The precipitate which formed was filtered to give 12 g (41%) of the crude amino ketone, mp 90–95°. Recrystallization from ethanol–water raised the melting point to 100–101° (lit.[16] mp 102°). The yields obtained with other substituents were *p*-CH_3, 64%; *p*-Br, 50%; *p*-$C(CH_3)_3$, 12%; and *p*-$CH(CH_3)_2$, 37%. In the case of the 4′-isopropyl and 4′-*tert*-butyl compounds, the amino ketone was isolated by extraction of the ammonium hydroxide solution with ether. Evaporation of the ether gave the amino ketones as viscous oils. These oils were converted directly to the azides, which were then purified.

2-Amino-4′-methoxybenzophenone. The DeTar procedure when used with anisole does not work due to cleavage of the anisole to phenol by the aluminum chloride. The following low-temperature modification gave the 2-amino-4′-methoxybenzophenone in low yield.

In 20 ml of anisole and 200 ml of ethylene chloride was dissolved 27 g (0.0925 mol) of *N*-toluenesulfonylanthranilic acid and 20.1 g (0.097 mol) of phosphorus pentachloride was added. The mixture was stirred and warmed for 30 min at 50°. The mixture was cooled in an ice bath and 53.6 g (0.43 mol) of anhydrous aluminum chloride added in four portions. The temperature was kept below 10° during the addition. After stirring for 6 hr in the ice bath, the mixture was decomposed with cold dilute hydrochloric acid. The solvent was removed under vacuum and the residue worked up as described in the general procedure above to give a crude solid, mp 66–75°. Recrystallization from aqueous ethanol gave 2.65 g (12.5%) of the amino ketone, mp 76.5–77.5° (lit.[17] mp 76.2–76.8°).

2-Azido-4′-substituted-benzophenones. In a typical procedure, 0.0185 mol of the amine was dissolved in 40 ml of concentrated hydrochloric acid and 40 ml of water was added. The mixture was cooled in an ice bath and diazotized with a solution of 0.02 mol of sodium nitrite in a minimum of water. After standing 30 min, the solution was filtered and to the filtrate was added dropwise 0.02 mol of sodium azide in a minimum of water. The solution was slowly allowed to warm to room temperature over a period of 2 hr. The solid azides were filtered and recrystallized from aqueous alcohol. Those that separated as oils were extracted out with ether, the ether evaporated, and the residue recrystallized. The yields and physical properties are given in Table I.[9] All of the 2-azidobenzophenones gave the expected peaks in the ir at 2100–2250 cm^{-1} for the azido group and at 1650–1670 cm^{-1} for the carbonyl group.

2-Methyl-4′-nitrobenzhydrol. The filtered Grignard reagent from 5.0 g (0.03 mol) of *o*-bromotoluene was cooled in a Dry Ice–methanol bath and to the solution was added dropwise 4.41 g (0.029 mol) of *p*-nitrobenzaldehyde dissolved in 100 ml of toluene. The reaction was stirred for 75 min after the addition was complete and then allowed to warm slowly to room temperature. Hydrochloric acid (6 *N*) was added to decompose any remaining Grignard reagent. The organic layer was removed, washed with bicarbonate, and dried over magnesium sulfate. Evaporation of the solvent gave a semisolid. It was dissolved in benzene and applied to an alumina (100 g) column. The first band was eluted with benzene and was unreacted *p*-nitrobenzaldehyde. The second band, eluted with 4:1 benzene:ether, gave 0.65 g of a viscous liquid. The third band, eluted with 1:1 benzene:ether, gave 0.39 g of a solid, mp 92–94°. This latter solid was identified as *p*-nitrobenzyl alcohol by conversion to its acetate derivative, mp 77–78° (lit.[18] 78°).

The second band was rechromatographed on alumina, this time eluting with 95:5 benzene:chloroform to give 0.336 g (48%) of 2-methyl-4′-nitrobenzhydrol as a viscous liquid. The infrared spectrum showed the expected peaks at 3500 (OH) and 1340 (NO_2) cm^{-1}. This material was used in the following oxidations.

Oxidation of 2-Methyl-4′-nitrobenzhydrol. In 25 ml of glacial acetic acid were dissolved 0.336 g (0.00138 mol) of the alcohol, 0.563 g (0.0056 mol) of chromium trioxide, and 2 ml of 85% phosphoric acid. The mixture was refluxed for 5 hr. The mixture was cooled and poured onto 20 g of ice. The solid was filtered, washed with water, and then heated with 25 ml of 5% sulfuric acid for 20 min on a steam bath. The light yellow solid was filtered and washed with water. On treatment with 5% sodium hydroxide, a portion of the solid dissolved. The base insoluble solid was filtered. Acidification of the filtrate gave white needles of 2-(4-nitrobenzoyl)benzoic acid. After recrystallization from ether–cyclohexane, 0.0879 g (23%), mp 198–200° dec, was obtained.

Anal. Calcd for $C_{14}H_9NO_5$: C, 62.15; H, 3.35; N, 5.17. Found: C, 61.92; H, 3.45; N, 5.18.

The base insoluble solid was dissolved in hot methanol and the solution cooled to give 0.081 g (21%) of white plates, mp 86.5–87.5°. The nmr spectrum showed a methyl singlet at 142 (3 H) cps, an A_2B_2 pattern at 496 (4 H) cps, and a multiplet at 474 (4 H) cps, indicating that the compound was 4-nitro-2′-methylbenzophenone.

Anal. Calcd for $C_{14}H_{11}NO_3$: C, 69.75; H, 4.59; N, 5.80. Found: C, 69.65; H, 4.54; N, 5.70.

Oxidation of 2-Methyl-4′-nitrobenzophenone. To 0.500 g (0.00207 mol) of 2-methyl-4′-nitrobenzophenone in 10 ml of acetic acid and 1 ml of water were added 0.63 g (0.00283 mol) of potassium dichromate and 0.6 ml of concentrated sulfuric acid. The mixture was heated on the steam bath for 1.5 hr. Work-up of the reaction as described above gave 0.291 g (52%) of 2-(4-nitrobenzoyl)benzoic acid. Only 0.071 g of the starting ketone was recovered.

2-(4-Nitrobenzoyl)benzamide. 2-(4-Nitrobenzoyl)benzoic acid was dissolved in 5 ml of thionyl chloride and the solution was refluxed for 5 hr. The excess thionyl chloride was removed under vacuum. The residue was cooled to −50° and 20 ml of liquid ammonia added. The ammonia was allowed to evaporate, and the residue was washed with water and then recrystallized from dimethylformamide to give a 95% yield of 2-(4-nitrobenzoyl)benzamide, mp 243–245° dec.

Anal. Calcd for $C_{14}H_{10}N_2O_4$: C, 62.20; H, 3.73; N, 10.39. Found: C, 62.40; H, 3.85; N, 10.60.

2-Amino-4′-nitrobenzophenone. 2-(4-Nitrobenzoyl)benzoic acid (0.268 g, 0.00099 mol) was refluxed for 1.5 hr with 10 ml of thionyl chloride. The excess thionyl chloride was removed under vacuum and the resulting crude acid chloride was dissolved in 10 ml of anhydrous acetone. To the stirred mixture in an ice bath was added 0.083 g (0.0011 mol) of sodium azide dissolved in 1 ml of water. After stirring 20 min, 20 ml of water was added. The resulting precipitate was filtered and allowed to air dry overnight, yield 0.253 g, mp 125–127° dec.

The dry azide was dissolved in 20 ml of dry benzene and refluxed for 2 hr. To the cooled solution was added 10 ml of concentrated hydrochloric acid. The benzene was evaporated under an air stream. The addition of ammonium hydroxide gave the crude product. Recrystallization from dioxane–water gave 0.20 g (84%) of needles, mp 153–153.5°.

Anal. Calcd for $C_{13}H_{10}N_2O_3$: C, 64.68; H, 4.15; N, 11.55. Found: C, 64.26; H, 4.32; N, 11.48.

Preparation of 3-(4-Nitrophenyl)anthranil by Hypobromite Oxidation. To an ice cold solution of 2.4 g of sodium hydroxide in 20 ml of water was added 0.6 ml of bromine. This solution was added to

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a suspension of 0.70 g (0.0026 mol) of 2-(4-nitrobenzoyl)benzamide in 10 ml of water containing an additional 2.4 g of sodium hydroxide. The suspension was heated at 70–80° for 20 min. The solution was cooled, and the solid which separated during the reaction was filtered and washed with water, yield 0.50 g (80%), mp 250–252°. Recrystallization from dimethyl sulfoxide raised the melting point to 252–254°. This solid gave no melting point depression with the 3-(4-nitrophenyl)anthranil formed by decomposition of 2-azido-4′-nitrobenzophenone. The infrared spectra were also identical.

Kinetic Studies. The rate of decomposition of the azides was determined by following the rate of evolution of nitrogen. The reaction vessel consisted of a single neck flask to which was attached a capillary side arm. In the reaction vessel was placed 35–60 ml of decalin. After temperature equilibration (±0.05°), the azide was added all at once and the vessel stoppered. The mixture was stirred rapidly by means of a magnetic stirrer located under the constant temperature bath. The evolved nitrogen was collected *via* the side arm which was connected to a gas buret. The reaction was allowed to proceed for a few minutes to reestablish thermal equilibrium and to overcome supersaturation effects before data were collected. The first order rate constants given in Table II were calculated from hand drawn plots. In Table III, a computer calculated least-squares fit of the data was used to obtain the rate constants.

2,3,4,5,6-Pentadeuterio-2′-nitrobiphenyl. In 20 ml of concentrated hydrochloric acid and 10 ml of water was dissolved 8.28 g (0.06 mol) of 2-nitroaniline. It was diazotized at 0° by the addition of 4.14 g (0.06 mol) of sodium nitrite in 10 ml of water. The solution was filtered into 10 g of benzene-d_6. The filter was washed with an additional 30 ml of water. To the filtrate was added 20 g of sodium acetate trihydrate. The solution was stirred vigorously for 48 hr. The benzene layer was removed and washed with acid and base. It was dried, concentrated, and then placed on an alumina column. Elution with benzene gave the product in the first band, yield 1.6 g (16%), mp 36–37° (lit.[19] 37°).

2,3,4,5,6-Pentadeuterio-2′-azidobiphenyl. In 15 ml of methanol was dissolved 1.5 g (0.0073 mol) of the nitro compound. To this was slowly added 7.25 g (0.035 mol) of stannous chloride dihydrate in 15 ml of concentrated hydrochloric acid. After heating on a steam bath for 45 min, the solution was poured into 150 ml of water. The solution was made strongly basic with sodium hydroxide solution and the amine was extracted out with ether. The ether was dried over magnesium sulfate and then evaporated to give 1.10 g (87%) of crude 2,3,4,5,6-pentadeuterio-2′-aminobiphenyl.

(19) See ref 18, p 427.

The crude aminobiphenyl (1.10 g, 0.0063 mol) was dissolved in 6 ml of concentrated hydrochloric acid and 8 ml of water and diazotized with 0.44 g (0.0063 mol) of sodium nitrite in 3 ml of water. After standing 20 min, 0.41 g (0.0063 mol) of sodium azide was added. After 1 hr, the azide was extracted with petroleum ether. The ether solution was washed with base and with water and then dried over magnesium sulfate. Evaporation of the solvent gave 0.5 g (40%) of the azide. After three recrystallizations from methanol, 0.25 g of the azide, mp 47–48° (lit.[20] 48–50°), was recovered.

Decomposition of 2,3,4,5,6-Pentadeuterio-2′-azidobiphenyl in Decalin and Hexadecane. The azide (0.25 g) was placed in 5.00 ml of decalin or hexadecane and the solution heated to 165–170° for 20 min, and then to be sure the reaction was complete, it was warmed to 185° for about 2 min. The solution was then cooled to room temperature and the precipitated carbazole was filtered and washed with a few drops of dry ligroin to remove most of the decalin or hexadecane. In some runs, the carbazole was recrystallized from ligroin before analysis. The decalin and hexadecane used were purified by extracting them with concentrated sulfuric acid, water, 5% sodium hydroxide, and water, followed by drying over magnesium sulfate, distilling, and finally drying for 1 month over molecular sieves.

The per cent N–H *vs.* N–D bonds was determined by dissolving the sample in dioxane and comparing the ratio of the intensity of N–H *vs.* N–D bands in the infrared spectrum with a series of standard samples prepared by mixing normal carbazole with *N*-deuteriocarbazole. The latter compound was prepared by shaking an ether solution of carbazole with several portions of heavy water in a separatory funnel. The dioxane used in the analysis was refluxed over sodium for 2 days, followed by distillation and drying over molecular sieves.

In order to correct for any loss of N–D during the procedure by exchange with moisture of the air, a sample of the *N*-deuteriocarbazole was run through the same procedure. After the correction was applied, the following results were calculated: decalin, 67 ± 5% N—D bonds, 33 ± 5% N–H bonds; hexadecane, 67 ± 5% N–D bonds, 33 ± 5% N–H bonds.

Acknowledgment. We would like to acknowledge the work of Mr. Alan Hansen who prepared the deuterated biphenyl compounds. Also we want to thank Dr. R. A. Abramovitch for his very helpful suggestions concerning the interpretation of the kinetic data.

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