Table V. Rate Constants and Arrhenius Parameters for the Reaction between Maleic Anhydride and Isoprene

Solvent (dielectric constant)	10^5k_1, l. mole^{-1} sec^{-1} (temp, °C)[a] 0	30.3	60.3	90.3	100.3	Arrhenius parameters, E kcal	10^5A l. mol^{-1}
Benzene (2.3)	1.62 (1.72)	17.5 (16.6)	104 (104)		762 (760)	12.3	1.20
Anisole (4.3)	2.59 (2.53)	25.2 (25.5)	166 (168)		1290 (1290)	12.6	3.07
Isopropyl ether (4.3)		5.01 (5.11)	43.8 (42.7)		411 (423)	14.2	8.70
Veratrole (4.5)		31.0 (31.2)	215 (208)	1010 (1010)		12.7	4.40
Chlorobenzene (5.6)	2.36 (2.36)	25.2 (23.9)	143 (157)		1220 (1200)	12.6	2.86
m-Dichlorobenzene (5.0)		33.0 (33.9)	230 (219)	992 (1040)		12.5	3.43
o-Dichlorobenzene (7.5)	7.62 (7.62)	66.7 (66.8)	367 (390)	1730 (1690)	2670 (2620)	11.8	2.12
Benzonitrile (26.5)	3.17 (3.17)	34.3 (34.6)	223 (241)	1225 (1220)		13.0	8.03
Nitrobenzene (36.1)	4.89 (4.89)	52.9 (47.0)	292 (295)		2220 (2150)	12.3	3.41
Nitromethane (39)	3.09 (3.20)	33.2 (30.8)	210 (193)		1330 (1410)	12.3	4.60

[a] Values in parentheses are calculated from the listed Arrhenius parameters. Initial concentration of each reactant was 0.5 *M*.

only about 10:1, and there is little correlation with the dielectric constant. Therefore although the reaction involves a rather polar dienophile, the transition state must be little more polar than the reactants. As one would expect on this basis the Arrhenius *A* factor varies little over the series; this makes the large variation reported by Fairclough and Hinshelwood[26] all the more puzzling. As yet, no other study of solvent effects as a function of temperature seems to have been reported.

The results listed in Table V may also be of interest in connection with the theory of solvent effects, representing as they do a set of accurate and consistent data for a homogeneous bimolecular reaction between neutral reagents, leading to neutral products, in a wide range of solvents.

The Photochemistry of Singlet and Triplet Azide Excited States[1a]

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Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. Received November 13, 1969

Abstract: The direct and photosensitized chemistry of a series of 2-azidobiphenyls has been studied. Direct excitation of 10^{-2} *M* solutions of the azides results in predominate formation of carbazoles accompanied by lower yields of azo compounds. The azo compound formation is quenched by dienes, oxygen, and pyrene with a resultant increase in carbazole yields. When acetone, acetophenone, benzophenone, or *m*-methoxyacetophenone were used to sensitize the decomposition of the azide, azo compounds were obtained. The quantum yield for the disappearance of 2-azidobiphenyl in the acetophenone-sensitized irradiation was found to be about 0.30. In contrast, aromatic hydrocarbons such as triphenylene, naphthalene, and pyrene sensitize the 2-azidobiphenyl with involvement of their respective singlet states; this leads to predominate formation of carbazole. Pyrene has been utilized in a unique sense. It functions to populate the azide excited singlet state by singlet energy transfer and also serves as a quencher for the excited triplet azide.

The thermolyses[2] of aromatic and aliphatic azides have attracted considerable attention in recent years. In many of these studies the nitrene in either its singlet or triplet state has been accepted as the reactive intermediate. Likewise in the direct excitation of azides by uv light the nitrene has been implicated as an important intermediate.[3,4]

In contrast to the thermolysis and direct photolysis results, investigations on the sensitized decomposition of azides have produced no consistent picture.[3e,j–l,5b,c] Thus it has been proposed that a triplet azide and probably a nitrene were intermediates in the aromatic hydrocarbon sensitized decomposition of triarylmethyl azides,[3g] while acetophenone-sensitized decomposition of ethyl azidoformate did not afford a triplet nitrene.[3j] Furthermore, the photosensitized decomposition of

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(1) (a) Part IV in this series. For preliminary reports: J. S. Swenton, *Tetrahedron Lett.*, 3421 (1968); J. S. Swenton, T. J. Ikeler, B. H. Williams, *Chem. Commun.*, 1263 (1969); (b) Sinclair Oil Fellow, 1966; (c) undergraduate research participant.

(2) For reviews of past literature, see R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, 64, 149 (1964); L. Horner and A. Christmann, *Angew. Chem.*, 75, 707 (1963).

(3) (a) A. Reiser, F. W. Willets, G. C. Terry, V. Williams, and R. Marley, *Trans. Faraday Soc.*, 64, 3265 (1968); (b) A. Reiser and R. Marley, *ibid.*, 64, 1806 (1968); (c) L. Horner, A. Christmann, and A. Gross, *Chem. Ber.*, 96, 399 (1963); (d) L. Horner, G. Bauer, and J. Dörges, *ibid.*, 98, 2631 (1965); (e) F. D. Lewis and W. H. Saunders, *J. Amer. Chem. Soc.*, 90, 7031 (1968); (f) *ibid.*, 7033 (1968); (g) *ibid.*, 89, 645 (1967); (h) W. H. Saunders and E. A. Caress, *ibid.*, 86, 861 (1964); (i) A. Mishra, S. N. Rice, and W. Lwowski, *J. Org. Chem.*, 33, 481 (1968); (j) J. S. McConaghy and W. Lwowski, *J. Amer. Chem. Soc.*, 89, 4450 (1967); (k) J. W. ApSimon and O. E. Edwards, *Can. J. Chem.*, 40, 896 (1962); (l) R. Moriarty and M. Rahman, *Tetrahedron*, 21, 2877 (1965).

(4) (a) G. Smolinsky, E. Wasserman, and W. A. Yager, *J. Amer. Chem. Soc.*, 84, 3220 (1962); 86, 3166 (1964); (b) A. Reiser, H. Wagner, and G. Bowes, *Tetrahedron Lett.*, 2635 (1966).

(5) For a discussion of radical induced decompositions of azides see (a) J. E. Leffler and H. H. Gibson, *J. Amer. Chem. Soc.*, 90, 4117 (1968); (b) M. T. Reagen and A. Nickon, *ibid.*, 90, 4096 (1968); (c) L. Horner and G. Bauer, *Tetrahedron Lett.*, 3573 (1966).

sulfonyl[5b] and acyl[8c,5c] azides in isopropyl alcohol occurred *via* a radical chain mechanism.

We report here our studies on the direct and sensitized decomposition of a series of 2-azidobiphenyls. Direct excitation yields a nitrene which subsequently cyclizes to carbazole, while ketone sensitization affords a long-lived species which yields azo-2-biphenyl (**3**). The utilization of aromatic hydrocarbons as sensitizers results in singlet not triplet energy transfer and thus yields carbazole as the major product.

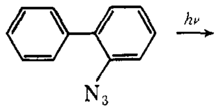
Direct Irradiation of 2-Azidobiphenyl. Direct irradiation of 2-azidobiphenyl produced carbazole (68–74%) and azo-2-biphenyl (8–12%). The yields of the two products were rather insensitive to the nature of the solvent (Table I). In addition there occurred no change in product yields when irradiations were done using a low-pressure mercury lamp (254 nm), a 350-nm source, or Pyrex filtered light from a 450-W medium-pressure mercury lamp.

Table I. Direct Irradiation of 2-Azidobiphenyl[a]

Run	Solvent	% carbazole	% azo compd
1	Benzene	71[b]	11[d]
2	Ether	74[b,c]	9[d]
3	Ether		9[d]
4	2-Propanol	68[b]	12[d]

[a] Pyrex filter, N_2 atmosphere, solutions $\sim 10^{-2}$ M in azide. [b] Yield by isolation. [c] Yield by vpc. [d] Yield by chromatography followed by uv analysis.

The structure of the azo compound was supported by analytical and spectroscopic data. The uv spectrum exhibited maxima at 458 nm (ϵ 410), 355 nm (ϵ 14,100), and 233 nm (ϵ 26,500) while the nmr showed only a broad singlet at τ 2.52. The mass spectral fragmentation pattern showed the parent ion at 334 (74%) and predominant fragmentation ions at 181 (21%), 153 (100%), and 152 (76%). The ions at 181 and 153, corresponding to loss of $C_{12}H_9$ and $C_{12}H_9N_2$ from the parent ion, result from processes well documented from the extensive investigations of Bowie, Lewis, and Cooks.[6] The ion at 152 may arise from loss of $C_{12}H_{10}N_2$ to yield the biphenylene species, $C_{12}H_8^+$. Complete confirmation of structure was obtained by hydrogenation of the azo compound to 2-aminobiphenyl.



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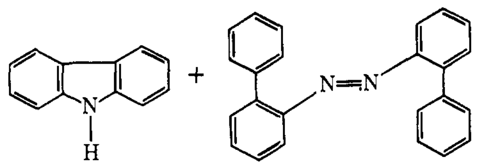

2 3

The low yield of azo compound in the direct irradiation of 2-azidobiphenyl and the lack of a suitable method of accurate product analysis at low conversion made quenching studies on the parent system difficult. Thus, we briefly examined a series of methoxy-substituted 2-azidobiphenyls[7] in order to obtain a more equitable yield of carbazole and azo compound on direct excitation. The results from the direct photolyses of 2′-, 3′-, and 4′-methoxy-2-azidobiphenyl are listed in Table II. In each case the major product from the irradiation was the respective carbazole(s),[8] while the azo compounds were produced in lesser amounts.[9] Since the methoxy-substituted azides offered no particular advantage over the parent system, further studies for the most part were carried out on **1**.

Table II. Direct Irradiation of Substituted 2-Azidobiphenyls[a]

Compound	% substituted carbazole(s)	% substituted azo compounds
2′-Methoxy	88	<3
3′-Methoxy	63[b]	16
4′-Methoxy	80	8

[a] Irradiations were performed in 1.5×10^{-2} M solutions of azide in 150 ml of ether under nitrogen using a Pyrex filter. [b] The average ratio from two runs of 1- to 3-methoxycarbazoles was 1.0.

Sensitization of 2-Azidobiphenyl. To obtain information on the multiplicity of the azide excited state responsible for carbazole and azo compound formation, sensitization studies were undertaken. Because of the known dependence of the triplet energy of biphenyl on the angle of twist between the rings,[10] our studies have dealt with high-energy ($E_T > 66$ kcal/mol) sensitizers. Tables III and IV record our results from the sensitized irradiations of the 2-azidobiphenyls. In contrast to the direct irradiations which afforded carbazoles as the major products, ketone-sensitized reactions led to the predominate formation of azo com-

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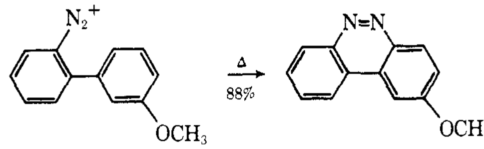
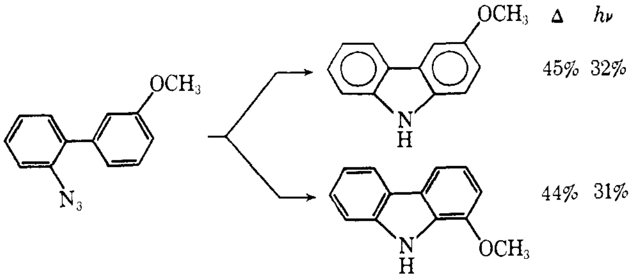
(6) J. H. Bowie, G. E. Lewis, and R. G. Cooks, *J. Chem. Soc., B*, 621 (1967).

(7) The methoxy-substituted azidobiphenyls were synthesized in a classical manner by treatment of the corresponding diazonium compound with aqueous sodium azide. In the case of the diazotization of 3′-methoxy-2-aminobiphenyl a second intramolecular reaction competed with azide formation. In the absence of sodium azide the second product was formed in 88% yield. On the basis of analytical and spectroscopic data (see Experimental Section) the product was tentatively assigned as 2-methoxybenzo[*c*]cinnoline. The latter would reasonably arise by diazo coupling at the position *para* to the methoxy group in accord with simple examples of azo coupling reactions.



(8) The 3′-methoxy-2-azidobiphenyl offered the possibilty of comparing the selectivity of the nitrene formed on direct irradiation with the nitrene generated *via* thermolysis. Interestingly, the ratio of the two isomeric carbazoles produced thermally and photochemically are virtually identical.



(9) The structural assignments of the substituted azo compounds rests on analytical and spectroscopic data as delineated in the Experimental Section.

(10) P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 2820 (1967).

Table III. Sensitized Irradiations of 2-Azidobiphenyl[a]

Run	Sensitizer (concn, M)	E_T, kcal/mol	% azo compd	% carbazole
1	Acetone (neat)[b]	>75	41	22
2	Acetophenone (1.7)[c]	74.6	40	<5
3	Acetophenone (3.4)[c]	74.6	49	*e*
4	Acetophenone (1.7)[d]	74.6	44	*e*
5	*m*-Methoxyacetophenone (1.4)[c]	72.4	39	*e*
6	Benzophenone (0.9)[c]	68.5	41	
7	Triphenylene (2.9×10^{-3})[c]	66.6	16	70

[a] Irradiations were performed on 1.7×10^{-2} M solutions of azide in 150 ml of benzene. [b] Rayonet reactor using RPR-3000 source. [c] Pyrex filter. [d] Rayonet reactor using RPR-3500 source. [e] The small amounts of carbazole formed prevented accurate yield data.

Table IV. Acetophenone-Sensitized Photolyses of Substituted 2-Azidobiphenyls[a]

Run	Compound	% substituted carbazole	% substituted azo compound
1	2′-Methoxy	*b*	49
2	3′-Methoxy	*b*	43
3	4′-Methoxy	8	43

[a] Irradiations were performed on 150 ml of 1.5×10^{-2} M solution of the azide in benzene using a Pyrex filter. [b] The small amounts formed prevented accurate isolation data.

pounds. The quantum yield of azide disappearance in the acetophenone sensitization was 0.30 ± 0.07 (8% conversion), indicative of a process of moderate efficiency.[11]

Initially it seemed unusual that while benzophenone (E_T = 68.5 kcal/mol) functioned as an adequate sensitizer for azo compound formation, triphenylene (E_T = 66.6 kcal/mol) did not.[12] Unfortunately, most aromatic ketones which are good sensitizers by virtue of their rapid and efficient intersystem crossing and high triplet energy are capable of hydrogen abstraction. Although it was considered unlikely that radicals generated by hydrogen atom abstraction were responsible for the azo compound formation in the ketone-sensitized runs, the different results with triphenylene were puzzling. To rule out sensitizer-derived radical intermediates as important species in our sensitizations, *m*-methoxyacetophenone was utilized as a sensitizer. It has been noted that *m*-methoxyacetophenone possesses the good qualities of efficient intersystem crossing and high triplet energy (E_T = 72.4 kcal/mol), but a low efficiency of photoreduction.[13] In our system, *m*-methoxyacetophenone sensitization of 2-azidobiphenyl proceeded in a fashion analogous to acetophenone itself which indicated no dependence of the reaction on hydrogen abstracting ability of the sensitizer.

The seemingly anomalous sensitization results recorded with triphenylene are most readily explained by assuming that under these conditions triphenylene transfers singlet energy rather than triplet energy to **1**. In order to show that triphenylene triplets were not involved in the azide sensitization, the triphenylene sensitization of the azide (1.8×10^{-2} M) was carried out in the presence of 0.2 M piperylene. If the triphenylene triplet state were involved in sensitization of **1**, piperylene ($E_T \sim 60$ kcal/mol) would compete with **1** for the triplet energy of triphenylene and thus slow the rate of azide decomposition. In fact it was found that piperylene did not alter the rate of triphenylene sensitization of **1**. In connection with quenching studies reported in the next section, it is apparent that naphthalene and pyrene also effect decomposition of **1** with involvement of their respective singlet states.[14] In view of these results it appears demanding to rigorously exclude singlet energy transfer when utilizing sensitizers which have slow rates of intersystem crossing.[16,17]

Quenching Studies. While the sensitization work had established the intermediacy of the excited azide triplet state in the formation of the azo compounds, quenching studies were undertaken to assess the merits of a triplet nitrene intermediate. If the triplet azide underwent loss of nitrogen to afford a triplet nitrene, suitable trapping agents might intercept this species before its reaction to form azo compound and thus yield a new addition product. On the other hand, if a triplet azide were the reactant, quenchers with a lower triplet energy than the azide would quench the azide triplet and lead to reduced yields of the azo compound.

The results of irradiation of 2-azidobiphenyl in the presence of various additives are presented in Table V. Molecules such as cyclooctene (E_T > 74 kcal/mol) and *cis*-dichloroethylene (E_T = >72 kcal/mol) markedly lower the yield of azo compound only when present at relatively high concentrations (runs 1–4). Unfortunately it was not possible to isolate and characterize any products arising from addition of a nitrene or azide linkage to the cyclooctene or *cis*-dichloroethylene. In contrast piperylene is much more effective in reducing the yield of azo compound since 0.2 M piperylene reduces the yield of azo compound to less than 1% (runs 7 and 8). At the same time irradiations in the presence of piperylene result in increased yields of carbazole. The effect is more dramatically illustrated in the case of the 3′-methoxy-2-azidobiphenyl (runs 11 and 12) where the carbazole yields increase from 63% in the direct irradiation to 98% in the presence of

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(11) The quantum efficiency of azide disappearance in the neat acetone sensitizations was 0.49 ± 0.08 (11% conversion) and 0.44 ± 0.10 (18% conversion). However, even though we had calculated acetone to absorb >99% of incident irradiation, carbazole always appeared to be formed. The carbazole may be formed by singlet energy transfer from acetone to the azide.

(12) In runs utilizing 2.9×10^{-2} M triphenylene and 1.7×10^{-2} M 2-azidobiphenyl light capture by the sensitizer was calculated to be between 60 and 75% and the carbazole yield was 70%. Using 0.12 M triphenylene and 1.8×10^{-2} M 2-azidobiphenyl (>90% light capture by triphenylene) the yield of carbazole was 74%.

(13) B. M. Monroe and S. A. Weiner, *J. Amer. Chem. Soc.*, **91**, 450 (1969).

(14) Indeed, there have been several recent reports of the involvement of hydrocarbon singlet states where the hydrocarbon triplet states had originally been supposed.[15]

(15) (a) S. L. Murov, R. S. Cole, and G. S. Hammond, *J. Amer. Chem. Soc.*, **90**, 2957 (1968); (b) R. S. Cooke and G. S. Hammond, *ibid.*, **90**, 2958 (1968); (c) P. D. Bartlett and P. S. Engel, *ibid.*, **90**, 2960 (1968).

(16) In principle the amount of singlet *vs.* triplet energy transfer should be dependent upon the concentration of the acceptor. At high acceptor concentrations singlet energy transfer (a bimolecular process) can compete with intersystem crossing (a unimolecular process). However, at a sufficiently low acceptor concentration intersystem crossing should compete effectively with singlet energy transfer.

(17) In this regard the exact correspondence in migratory aptitudes from direct and photosensitized photolysis of triarylmethyl azides observed by Lewis and Saunders[3g] may be explained by singlet energy transfer. In fact, recently it has been shown that aromatic hydrocarbon singlets are deactivated by alkyl azides: F. D. Lewis and J. C. Dalton, *J. Amer. Chem. Soc.*, **91**, 5260 (1969).

Table V. Irradiation of 2-Azidobiphenyl in the Presence of Additives

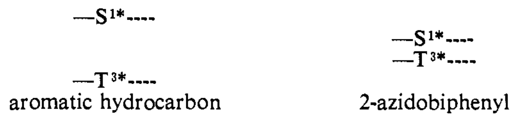
Run	Compound	Conditions	% carbazole	% azo compound
1	2-Azidobiphenyl	Cyclooctene (0.2 *M*), benzene^a	81	10
2	2-Azidobiphenyl	Cyclooctene (2.0 *M*), benzene^a	83	<1
3	2-Azidobiphenyl	*cis*-1,2-Dichloroethylene (0.2 *M*), benzene^a	78	5.6
4	2-Azidobiphenyl	*cis*-1,2-Dichloroethylene (2.0 *M*), benzene^a	72	<2
5	2-Azidobiphenyl	Naphthalene (0.21 *M*), benzene^{a,d}	67	6
6	2-Azidobiphenyl	O_2 (saturated), benzene^b	80	<1
7	2-Azidobiphenyl	Piperylene (2.0 *M*), ether^{b,c}	89	<1^c
8	2-Azidobiphenyl	Piperylene (0.2 *M*), ether^b	84	<2
9	2-Azidobiphenyl	Pyrene (1.7×10^{-2} *M*), benzene^{a,d}	94	<2
10	2-Azidobiphenyl	Pyrene (1.3×10^{-2} *M*), benzene^{a,d}	90	<3
11	3′-Methoxy-2-azidobiphenyl	Piperylene (3.6 *M*), ether^{d,e}	98	<1
12	3′-Methoxy-2-azidobiphenyl	Piperylene (0.5 *M*), ether^{d,e}		<2

[a] Rayonet RPR-3500 source. [b] Hanovia 450-W medium-pressure source, Pyrex filter. [c] The yield of 4% reported earlier was high apparently due to the difficulty in analysis of the small amount formed. [d] Significant percentage of light capture by the aromatic hydrocarbon. [e] The two carbazoles were formed in a 1:1 ratio.

piperylene.[18] Surprisingly, even dissolved oxygen markedly reduces the yield of azo compound. The reduction of azo compound yield in the presence of olefins and dienes in our system could involve either energy transfer from excited azide, chemical reaction with a nitrene or excited azide, or both of these processes.

Owing to possible ambiguities in interpreting the quenching action of piperylene and oxygen, we sought other molecules possessing low triplet energies yet nonolefinic or free radical in character. Since the choice of quenchers other than dienes was severely limited due to light absorption by the quenchers, we have used naphthalene and pyrene in a dual role. In view of the singlet sensitization noted with triphenylene, it was only necessary to choose an aromatic hydrocarbon capable of singlet sensitization yet having a sufficiently low triplet energy to quench the 2-azidobiphenyl triplet as illustrated in Scheme I. Our initial work involved a solution of 0.2 *M* naphthalene (E_T = 61 kcal/mol) where it was estimated that at this concentration naphthalene was absorbing 40–60% of the incident irradiation. Under these conditions both the carbazole and azo compound yield showed only a small decrease (run 5). Inspection of tables of sensitizers[19] showed pyrene (E_T = 48.7 kcal/mol) as one of the few aromatic hydrocarbons possessing a triplet energy below naphthalene. Utilizing pyrene concentrations to effect greater than 85% absorption of the incident irradiation led to increased yields of carbazole at the expense of azo compound yield. The observation that naphthalene does not affect the yield of azo compound whereas pyrene shows quenching is most reasonably explained on the basis of quenching of an azide excited state.

Scheme I



Discussion

The singlet chemistry of the 2-azidobiphenyl is without complication. Direct excitation leads to loss of nitrogen forming a nitrene which subsequently cyclizes to yield carbazole. Reiser and coworkers[4b] have detected the triplet nitrene from photolysis of 2-azidobiphenyl at 77°K and have shown that on warming the solution carbazole was produced. However, the workers could not exclude partial or complete reaction from a singlet intermediate formed *via* the triplet. Thus the spin state of the nitrene leading to carbazole still remains an open question, although our results appear more consistent with a singlet nitrene.

There is certainly more than one mechanism for azo compound formation as judged by the diverse yield of azo compounds recorded in the chemical literature for various systems.[3c,20a,b] The sensitization studies reported here implicate the 2-azidobiphenyl triplet as one of the intermediates in azo compound formation. It is also plausible that the quenching effect on azo compound formation noted with piperylene and pyrene are due to deactivation of the azide triplet state. However, the quenching effect noted with oxygen, cyclooctene, and *cis*-dichloroethylene could very likely involve reaction with an intermediate (*i.e.*, excited azide or nitrene). Since experimental difficulties prevented accurate measurement of quenching rate constants, we cannot exclude the possibility that all quenching in fact involves chemical reaction with an intermediate such as a nitrene.[21] Furthermore, Reiser and coworkers[3a] have shown that both aromatic triplet nitrenes and excited aromatic azides (unspecified multiplicity) react with ground state azide at a diffusion-controlled rate. Thus kinetically both species are likely candidates for the azo compound formation. The last point bearing mention is that of isolable intermediates in these reactions. Following the course of reaction by tlc as well as changing the wavelength and intensity of

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(18) Although quenching studies of the Stern–Volmer type would be very informative in this system, good analytical procedures for the azo compound in low conversion irradiations were not available to us.

(19) J. G. Calvert and J. N. Pitts, "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 298.

(20) (a) Reference 2a, p 160; (b) G. Smolinsky, *J. Org. Chem.*, 26, 4108 (1961).

(21) Interesting observations have been reported on the change in product distribution of nitrenes in the presence of various radical traps: D. S. Breslow and E. I. Edwards, *Tetrahedron Lett.*, 2123 (1967). These workers noted that radical traps such as *m*-dinitrobenzene alter the ratio of reduction to insertion products in the pyrolysis of ethyl and *n*-octadecyl azidoformate in cyclohexane. In general the effect for a series of additives was to increase the amount of insertion product (ascribed to singlet nitrene reacting) at the expense of the abstraction product (ascribed to triplet nitrene reacting).

the exciting light did not suggest the presence of any stable intermediate in the azide sensitizations.

Experimental Section

Ir spectra were recorded with a Perkin-Elmer Infracord Model 137 spectrometer. Uv spectra were determined with a Cary 14 recording spectrometer. Unless otherwise noted, nmr spectra were measured on a Varian A-60 spectrometer. The mass spectra were measured with an AEI MS-9 mass spectrometer at an ionizing voltage of 70 eV. Photolyses were carried out with a Hanovia 450-W medium-pressure source in a stirred reactor in a purified nitrogen atmosphere unless otherwise noted. Vapor phase analysis for carbazole was determined on a Varian Model 1200 flame ionization gas chromatograph using fluorenone as internal standard (5 ft × $^1/_8$ in. 5% SE-30 on Var-A-Port 30 at 170°). All elemental analyses were determined by Scandinavian Microanalytical Laboratory, Herlev, Denmark, on sublimed samples.

2-Nitrobiphenyls. All the methoxy-2-nitrobiphenyls utilized in this work were known. These were conveniently prepared in 60–70% yield by condensation of the appropriate iodomethoxybenzene with *o*-bromonitrobenzene using copper–bronze.[22]

2-Aminobiphenyls. The methoxy-2-aminobiphenyls were prepared in >90% yield by hydrogenation of the corresponding nitro compounds in 95% ethanol using 5% Pd–C as catalyst. The physical properties were in agreement with published values.

2-Azidobiphenyl and 2′-Methoxy-2-azidobiphenyl. These compounds were prepared by procedure A of Smith and Brown. The 2-azidobiphenyl had mp 48–49° (lit.[23] mp 49–50°). The 2′-methoxy-2-azidobiphenyl was obtained in 75% yield, mp 46–47° (lit.[24] mp 48°).

4′-Methoxy-2-azidobiphenyl. The 4′-methoxy-2-aminobiphenyl was converted to the corresponding azide using procedure A of Smith and Brown.[23] The crude material was recrystallized three times from methanol to afford an 80% yield of pure azide, mp 43–44°.

Anal. Calcd for $C_{13}H_{11}N_3O$: C, 69.32; H, 4.92; N, 18.66. Found: C, 69.07; H, 5.03; N, 18.22.

3′-Methoxy-2-azidobiphenyl. Conversion of 3′-methoxy-2-aminobiphenyl to the azide using the general procedure afforded the azide as a greenish oil. Purification of the crude azide by silica gel chromatography using hexane as eluent afforded a 60% yield of a viscous clear oil showing the expected azide absorption in the ir.

Anal. Calcd for $C_{13}H_{11}N_3O$: C, 69.32; H, 4.92; N, 18.66. Found: C, 69.67; H 4.98; N, 18.53.

2-Methoxybenzo[*c*]cinnoline. A cooled, stirred solution of 1.0 g (5.03 mmol) of 3′-methoxy-2-aminobiphenyl in 1.2 ml of concentrated sulfuric acid and 7 ml of water was diazotized by dropwise addition of 0.6 g of sodium nitrite in 5 ml of water. After removal of excess nitrous acid with urea the solution was allowed to warm to room temperature. After stirring for 1 additional hr the yellow solid which formed was collected, 0.88 g, mp 142–145°. Further purification by silica gel chromatography using ether as eluent afforded 0.74 g of light yellow solid. After sublimation under oil pump vacuum at 100° followed by recrystallization from methanol there was obtained 0.72 g (72%) of yellow needles: mp 148–149°; uv max (95% EtOH) 322 nm (ϵ 11,500), 252 nm (ϵ 36,200), and 246 nm (ϵ 37,400); nmr (CCl_4) τ 5.98 (s, 3 H), and two sets of highly structured absorptions at 2.0–2.7 (3 H) and 1.2–1.7 (4 H); mass spectrum, *m/e* (relative intensity) 210 (parent, 100), 167 (35), and 139 (98).

Anal. Calcd for $C_{13}H_{10}N_2O$: C, 74.27; H, 4.79; N, 13.31. Found: C, 74.21; H, 4.81; N, 13.35.

Direct Photolysis of 2-Azidobiphenyl. The following procedure was typical of that used throughout this work. The azide, 0.5024 g (2.58 mmol), was dissolved in 150 ml of benzene and the solution was purged with purified nitrogen for 0.5 hr. After irradiation for 1 hr the solvent was removed on the rotary evaporator and the resulting dark solid was dissolved in a minimum amount of acetone (*ca.* 15 ml). The acetone solution was added to *ca.* 1 g of silica gel and the acetone was carefully removed on the rotary evaporator. The resulting solid consisting of reaction mixture impregnated on silica gel was placed on top of a 55 × 2.4 cm column of silica gel slurry packed in 1% ether–hexane. Elution was as follows: 1% ether–hexane, 0.5 l., nil; 2% ether–hexane, 0.5 l., 0.0494 g (0.148 mmol, 12%) of azo-2-biphenyl; 2% ether–hexane, 0.25 l., 0.0143 g of unidentified red oil; 10% ether–hexane, 0.5 l., nil; 10% ether–hexane, 1 l., 0.3054 g (1.83 mmol, 71%) of carbazole as yellow plates. Continued elution with higher polarity solvent mixtures yielded dark oils which resisted crystallization. The purity of the azo-2-biphenyl and carbazole was established by tlc and ir. Due to the small amount of azo compound obtained in direct irradiation and contamination with small amounts of azide in some runs, the azo fraction was analyzed by uv (95% ethanol) at 450 nm. Analysis of the azo chromatographic fraction indicated 0.047 g (0.142 mmol) of azo-2-biphenyl.

Irradiation of 2-Azidobiphenyl and Pyrene at 3500 Å. A mixture of 0.409 g (2.1 mmol) of 2-azidobiphenyl and 4.354 g (21.5 mmol) of purified pyrene in 130 ml of benzene was irradiated under nitrogen for 5 hr with a bank of 16 RPR-3500 lamps. The yield of carbazole was determined by vpc as 84%, while the yield of azo compound, 2%, was obtained by uv analysis of the eluent from silica gel chromatography of the reaction mixture. A duplicate determination from irradiation of 4.045 g of pyrene and 0.510 g of 2-azidobiphenyl showed a 92% yield of carbazole by vpc.

Irradiation of 2-Azidobiphenyl and Naphthalene at 3500 Å. By a procedure analogous to that above 0.501 g (2.56 mmol) of 2-azidobiphenyl and 3.17 g (25.9 mmol) of naphthalene in 150 ml of benzene was irradiated for 3.5 hr. Vpc analysis for carbazole showed 67%, while uv analysis of the eluent from silica gel chromatography of the reaction mixture indicated the yield of azo compound as 6%. In a duplicate determination the vpc yield of carbazole was 66%.

Triphenylene Sensitization of 2-Azidobiphenyl at 3500 Å. A Pyrex test tube containing 0.0521 g (0.27 mmol) of 2-azidobiphenyl and 0.4253 g (1.86 mmol) of triphenylene in 15 ml of benzene was purged with nitrogen and irradiated for 5 hr with a bank of 16 RPR-3500 lamps. The carbazole yield by vpc was 74%.

Preparative Irradiation of 2-Azidobiphenyl and Triphenylene. A mixture of 0.501 g (2.57 mmol) of 2-azidobiphenyl and 1.008 g (4.37 mmol) of triphenylene in 150 ml of benzene was irradiated for 1 hr. Chromatography on silica gel afforded a 70% yield of carbazole. The azo compound yield as determined by uv analysis of the eluent of chromatography of the reaction mixture was 16%.

Acetophenone-Sensitized Irradiation of 2-Azidobiphenyl. This general procedure was utilized throughout this work for acetophenone sensitizations. The azide, 1.53 g (7.8 mmol), and 70 ml of acetophenone were diluted to 150 ml with benzene. The stirred solution was purged for 0.5 hr with purified nitrogen and then irradiated for 3 hr (a 450-W lamp) with a Pyrex filter. Removal of the benzene on the rotary evaporator followed by short-path distillation of the acetophenone (40°, 0.1 mm) afforded a dark solid which was chromatographed on a 2 × 72 cm silica gel column slurry-packed with 1% ether–hexane. Elution proceeded as follows: 1% ether–hexane, 0.5 l., nil; 1% ether–hexane, 2 l., 0.6405 g (0.384 mmol, 49%) of azo-2-biphenyl. Continued elution with higher polarity solvents yielded only a trace of carbazole and dark viscous unidentified oils.

The material obtained from the column was a yellow-orange amorphous solid which began softening and turning red at 120° and completely melted at 143–144°. Slow recrystallization of this material from ethanol afforded red crystals, 0.52 g, melting sharply at 144.5–145.5°. The two forms showed identical tlc retention times, ir (CS_2), and uv spectra making it unlikely that they were *cis* and *trans* isomers: ir (CS_2) strong absorptions at 12.97, 13.05, 13.60, and 14.40 μ; nmr (CCl_4) τ 2.52 (s); uv max (95% EtOH) 458 nm (ϵ 410), 335 nm (ϵ 14,100), and 233 nm (ϵ 26,500); mass spectrum, *m/e* (relative intensity) 334 (parent, 74), 333 (28), 181 (20), 154 (18), 153 (100), 152 (76), 151 (18).

Anal. Calcd for $C_{24}H_{18}N_2$: C, 86.20; H, 5.43; N, 8.38. Found: C, 86.27; H, 5.47; N, 8.39.

Sensitized Irradiation of 2-Azidobiphenyl at 3500 Å. A mixture of 0.50 g (2.56 mmol) of 2-azidobiphenyl and 25.0 g of acetophenone was diluted to 100 ml with benzene and this solution was transferred to four 0.8 × 14 cm Pyrex test tubes. After purging with nitrogen the tubes were irradiated in a merry-go-round apparatus for 210 min using a bank of 16 RPR-3500 lamps (spectral output from 310 to 410 mμ, New England Ultraviolet Co., Middletown, Conn.). Tlc analysis throughout the reaction indicated the formation of only azo compound. Chromatography in the usual manner yielded 0.210 g of crude azo compound. Uv analysis of this fraction indicated 0.190 g (0.57 mmol, 45%) of azo-2-biphenyl.

Hydrogenation of Azo-2-biphenyl. The azo compound, 0.100 g (0.30 mmol), was dissolved in 50 ml of methanol and hydrogenated at 60 psi for 3 hr using 0.05 g of platinum oxide as catalyst.

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(22) P. E. Fanta, *Chem. Rev.*, 64, 613 (1964).

(23) P. A. S. Smith and B. B. Brown, *J. Am. Chem. Soc.*, 73, 2435, 2438 (1951).

(24) G. Smolinsky, *ibid.*, 83, 2489 (1961).

Removal of the catalyst and distillation of the methanol afforded a virtually quantitative yield of 2-aminobiphenyl as identified by comparison of ir and nmr spectra with authentic material.

Photolysis of 2-Azidobiphenyl in Oxygen Saturated Benzene. A solution of 0.5291 g (2.61 mmol) of 2-azidobiphenyl in 150 ml of benzene was purged for 1 hr with pure oxygen and then irradiated for 1 hr through Pyrex with a stream of oxygen bubbling through the solution. Inspection of the light yellow photolysis solution by tlc (10% ether–hexane) indicated only a trace of azo compound. (The plate was developed by spraying with concentrated sulfuric acid.) Chromatography of the photolysis product on silica gel in the usual fashion afforded 0.3481 (2.08 mmol, 80%) of carbazole as white plates.

Photolysis of Azo-2-biphenyl in Oxygen Saturated Benzene. In a procedure analogous to the above 0.1001 g (0.30 mmol) of azo-2-biphenyl was irradiated for 1 hr. Thin layer analysis (100% hexane) of the reaction mixture indicated azo compound contaminated by a trace of material having one-third the R_f value as the azo compound. Recrystallization of the residue after removal of solvent afforded 0.0867 g of azo compound as identified by ir (CS_2).

Sensitized Irradiation of Azo-2-biphenyl. Irradiation of a mixture of 0.50 g of azo-2-biphenyl and 31.6 g of acetophenone diluted to 150 ml with benzene was carried out for 1 hr under a nitrogen atmosphere. Removal of the benzene and acetophenone by distillation yielded a reddish solid which showed an ir identical with starting azo-2-biphenyl. Analysis of the material by uv using the 450-nm band showed 0.48 g (96% recovery) of the starting azo compound.

Direct Irradiation of 2′-Methoxy-2-azidobiphenyl. The azide, 0.505 g (2.24 mmol), was stirred and irradiated in 150 ml of ether through Pyrex for 1 hr. Chromatographic separation of the products was carried out on a 2 × 72 cm column slurry-packed in 2% ether–hexane. Elution proceeded as follows: 2% ether–hexane, 0.4 l., nil; 5% ether–hexane, 0.5 l., nil; 10% ether–hexane, 0.4 l., nil; 15% ether–hexane, 0.8 l., 0.096 g of azo-2-(bis-2′-methoxy)-biphenyl; 15% ether–hexane, 1.4 l., 0.388 g of 4-methoxycarbazole as a tan solid. Recrystallization of the 4-methoxycarbazole from hexane–methylene chloride gave pale yellow crystals, mp 134–136° (lit.[24] mp 135–136°).

Sensitized Irradiation of 2′-Methoxy-2-azidobiphenyl. A mixture of the azide, 0.505 g (2.24 mmol), and 31.6 g of acetophenone was diluted to 150 ml with benzene and irradiated for 1 hr through Pyrex. After removal of the benzene and acetophenone the reaction mixture was chromatographed on a 2 × 72 cm silica gel column slurry-packed with 2% ether–hexane. Elution proceeded as follows: 0.4 l. each of 2%, 5%, 10%, and 15% ether–hexane, nil; 2 l., 25% ether–hexane, 0.216 g (49%) of azo-2-(bis-2′-methoxy)-biphenyl. Elution with higher polarity solvent yielded no additional crystalline products. Recrystallization of the azo fractions from 2-butanone yielded orange crystals: mp 230–232°; ir (KBr) 6.23 (w), 6.69 (w), 6.79 (w), 6.87 (w), 6.92 (w), 7.01 (w), 7.28 (w), 7.82 (w), 8.03 (m), 8.13 (w), 8.48 (w), 8.68 (w), 8.91 (w), 9.51 (w), 9.79 (w), 12.60 (w), 12.88 (w), 12.95 (w), 13.05 (m), 13.30 (s), and 13.61 μ (w); uv max ($CHCl_3$) 450 nm (ϵ 351), 323 nm (ϵ 14,500); a minimum of 288 nm (ϵ 10,900) was followed by strong end absorption; mass spectrum, m/e (relative intensity) 394 (parent, <2), 364 (29), 363 (100), 183 (17), 168 (78).

Anal. Calcd for $C_{26}H_{22}N_2O_2$: C, 79.16; H, 5.62; N, 7.10. Found: C, 78.96; H, 5.66; N, 7.29.

Direct Irradiation of 3′-Methoxy-2-azidobiphenyl. The azide, 0.505 g (2.24 mmol), in 150 ml of ether was stirred and irradiated through a Pyrex filter for 1 hr. Chromatography on silica gel using a 2 × 72 cm column slurry-packed in 2% ether–hexane yielded the following fractions: 0.4 l. of 2%, 5%, 10%, and 15% ether–hexane, nil; 0.4 l., 15% ether–hexane, 0.153 g (34%) of 1-methoxycarbazole as light tan crystals; 1.6 l., 15% ether–hexane, 0.070 g (17%) of azo-2-(bis-3′-methoxy)biphenyl as an orange solid; 0.2 l., 20% ether–hexane, nil; 1.2 l., 20% ether–hexane, 0.130 g of 3-methoxycarbazole as light tan crystals. Recrystallization of the 1-methoxycarbazole from methanol yielded 0.060 g of pure material, mp 68–69.5° (lit.[25] mp 69–70°). Vpc analysis of the mother liquors (5 ft × 0.25 in., 5% SE-30 on 60–80 Chromosorb W, 180°) using carbazole as an internal standard showed 0.060 g of 1-methoxycarbazole to be present. The 3-methoxycarbazole fractions were recrystallized from methanol to yield 0.102 g of white crystals, mp 151–152° (lit.[26] mp 151–152°).

Irradiation of 3′-Methoxy-2-azidobiphenyl with Piperylene. The azide, 0.505 g (2.24 mmol), was dissolved in a mixture of 96.5 ml of ether and 53.5 ml of freshly distilled piperylene and irradiated through a Pyrex filter for 1 hr. Chromatography of the reaction mixture as in the direct irradiation afforded only a trace of azo compound, 0.200 g (45%) of 1-methoxycarbazole (crude mp 66–68°), and 0.196 g (44%) of 3-methoxycarbazole (crude mp 147–150°).

A second run made with 0.505 g (2.24 mmol) of azide and 7.4 ml of piperylene in 143 ml of ether afforded less than 2% of the azo-2-(bis-3′-methoxy)biphenyl.

Thermal Decomposition of 3′-Methoxy-2-azidobiphenyl. The azide, 0.505 g (2.24 mmol), was dissolved in 50 ml of *o*-dichlorobenzene and heated at 150° for 3 hr. Removal of the solvent by vacuum distillation followed by chromatography on silica gel in the usual manner yielded 0.215 g (48%) of 1-methoxycarbazole (crude mp 68–70°) and 0.220 g (49%) of 3-methoxycarbazole (crude mp 150–151°).

Sensitized Irradiation of 3′-Methoxy-2-azidobiphenyl. A mixture of the azide, 0.505 g (2.24 mmol), and 31.6 g of acetophenone was diluted to 150 ml with benzene and irradiated for 1 hr using a Pyrex filter. Removal of the solvent and the acetophenone by distillation yielded a dark solid, which was chromatographed on a 2 × 72 cm column slurry-packed with 2% ether–hexane. Elution proceeded as follows: 0.2 l. of 2%, 5%, 10%, 15% ether–hexane, nil; 0.2 l., 15% ether–hexane, 0.023 g of unidentified liquid; 1.6 l., 15% ether–hexane, 0.198 g of azo-2-(bis-3′-methoxy)biphenyl as a red solid. Continued elution with higher polarity solvent mixtures afforded small amounts of unidentified dark viscous oils. The azo-2-(bis-3′-methoxy)biphenyl was recrystallized from hexane to afford 0.151 g of orange crystals: mp 124–125°; ir (KBr) 6.24 (s), 6.80 (s), 6.88 (w), 6.96 (w), 7.09 (w), 7.58 (m), 7.69 (w), 7.89 (m), 8.01 (m), 8.20 (s), 8.48 (w), 9.66 (w), 9.81 (w), 10.45 (w), 11.25 (w), 11.40 (m), 11.62 (s), 12.32 (w), 12.60 (s), 12.90 (s), 13.26 (s), and 14.30 μ (s); uv (95% EtOH) distinct maxima at 450 nm (ϵ 503) and 328 nm (ϵ 14,400) followed by strong end absorption with visible shoulders at 250 nm (ϵ 20,000) and 210 nm (ϵ 62,000). The mass spectrum showed a large number of fragmentation peaks in the region m/e 127–211; only the most prominent are listed: m/e (relative intensity) 394 (parent 68), 211 (90), 199 (100), 197 (70), 183 (58), 182 (60), 168 (70), 154 (58), 139 (55), and 127 (30).

Anal. Calcd for $C_{26}H_{22}N_2O_2$: C, 79.16; H, 5.62; N, 7.10. Found: C, 78.96; H, 5.66; N, 7.29.

Direct Irradiation of 4′-Methoxy-2-azidobiphenyl. The azide, 0.500 g (2.22 mmol), in 150 ml of ether was stirred and irradiated through Pyrex for 1 hr. Chromatography on silica gel using a 2 × 72 cm column slurry-packed in 2% ether–hexane yielded the following fractions: 0.4 l., 2%, 5%, 10%, and 15% ether–hexane, nil; 1.2 l., 20% ether–hexane, 0.034 g of azo-2-(bis-4′-methoxy)-biphenyl as an orange solid; 1.0 l., 20% ether–hexane, 0.117 g of 2-methoxycarbazole as light yellow plates; 2.2 l., 30% ether–hexane, 0.281 g of 2-methoxycarbazole. Recrystallization of the carbazole fractions from methanol yielded 0.305 g of nearly white plates, mp 238–240° (lit.[27] mp 235–236°).

Sensitized Irradiation of 4′-Methoxy-2-azidobiphenyl. A mixture of the azide, 0.505 g (2.24 mmol), and 31.6 g of acetophenone was diluted to 150 ml with benzene and irradiated for 1 hr through Pyrex. Distillation of the benzene and acetophenone yielded a dark solid. Trituration of the dark solid with acetone resulted in crystallization of azo-2-(bis-4′-methoxy)biphenyl as an orange solid, 0.170 g, mp 233–244°. Chromatography of the mother liquors afforded an additional 0.025 g of the azo compound for a crude yield of 44%. Recrystallization of the compound from 2-butanone yielded 0.169 g of orange needles: mp 237–238°; ir (KBr) 6.23 (m), 6.67 (m), 6.86 (m), 6.99 (w), 7.79 (m), 7.92 (m), 8.06 (s), 8.52 (m), 9.08 (w), 9.62 (w), 9.77 (m), 9.91 (w), 10.07 (w), 12.12 (s), 12.90 (m), 12.99 (m), and 13.21 μ (s); uv max ($CHCl_3$) 326 nm (ϵ 11,900) and 251 nm (ϵ 26,900) in addition to shoulders at approximately 450 nm (ϵ 690) and 256 nm (ϵ 10,800); mass spectrum, m/e (relative intensity) 394 (parent, 100), 393 (43), 379 (15), 211 (22), 198 (20), 184 (18), 183 (96), 168 (58), 152 (20), 140 (32), 139 (31).

Anal. Calcd for $C_{26}H_{22}N_2O_2$: C, 79.16; H, 5.62; N, 7.10. Found: C, 79.02; H, 5.69; N, 7.12.

Quantum Yield for Disappearance of 2-Azidobiphenyl. The quantum yield of azide disappearance was measured by irradiating 13.5 ml of a 1.6×10^{-2} *M* acetone solution of 2-azidobiphenyl in a

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(25) D. P. Chakraborty, B. K. Barman, and P. K. Bose, *Tetrahedron*, 21, 681 (1965).

(26) A. H. Milne and M. L. Tomlinson, *J. Chem. Soc.*, 2789 (1952).

(27) C. K. Bradsher, F. C. Brown, and P. H. Leake, *J. Org. Chem.*, 22, 500 (1957).

quartz test tube using 16 RPR-3000 lamps in a merry-go-round apparatus. The solution was purged with prepurified nitrogen prior to irradiation. Measurement of the light intensity was made by simultaneously irradiating a 0.15 *M* solution of potassium ferrioxalate.[28] The irradiated solution was analyzed by vpc using 9-fluorenone or dimethyl diphenate as internal standards. Under conditions of the vpc analysis no decomposition of the azide was noted [Varian Aerograph Model 1200 flame ionization vpc, 5 ft × $^1/_8$ in. 5% SE-30 on 100–120 mesh Var-A-Port 30, injector 170°, column 160°] (see Table VI).

In an analogous fashion 14 ml of a benzene solution of 2-azidobiphenyl (1.85 × 10^{-2} *M*) and acetophenone (2.02 *M*) was irradiated with a bank of 16 RPR-3000 lamps while simultaneously irradiating an actinometer solution. The quantum yield for azide disappearance (8% conversion) was found to be 0.30 ± 0.07 (0.0686 mequiv absorbed).

Table VI

2-Azidobiphenyl consumed, mmole	Mequiv absorbed	% conversion	Φ
2.05 × 10^{-2}	4.84 × 10^{-2}	11	0.49
3.45 × 10^{-2}	9.12 × 10^{-2}	19	0.44

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[28] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **235**, 518 (1956).

The Heats of Combustion and Strain Energies of Bicyclo[*n*.*m*.0]alkanes

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Abstract: The heats of combustion, vapor pressures, and liquid heat capacities of a number of bicyclic alkanes have been determined. The derived liquid and gas heats of formation in kilocalories mole^{-1} at 25° are as follows: *cis*-bicyclo[3.1.0]hexane, 1.3 ± 0.7, 9.3 ± 0.8; *cis*-bicyclo[4.1.0]heptane, −8.7 ± 0.8, 0.4 ± 1.0; *cis*-bicyclo[5.1.0]-octane, −14.2 ± 0.5, −3.8 ± 0.7; *cis*-bicyclo[6.1.0]nonane, −19.4 ± 0.8, −7.6 ± 1.0; *cis*-bicyclo[4.2.0]octane, −16.3 ± 0.8, −6.1 ± 1.1; *cis*-bicyclo[3.3.0]octane, −32.6 ± 0.3, −22.3 ± 0.5; *trans*-bicyclo[3.3.0]octane, −26.1 ± 0.4, −15.9 ± 0.6; *cis*-bicyclo[5.3.0]decane, −43.9 ± 0.9, −31.1 ± 1.2. Experimental strain energies are derived from group contributions. Strain energies and geometries are also calculated by energy minimization with a set of transferable valence force potential functions. The agreement of calculated and experimental strain energies is satisfactory. The gas phase thermodynamic functions (free energy and enthalpy functions, heat capacity, and entropy) are also calculated.

In view of the great interest in recent years in the chemistry of strained cyclic hydrocarbons, studies of molecular properties and structure of such compounds are greatly in need. Of particular importance is the desirability of obtaining heats of formation from which empirical strain energies may be derived. It is the purpose of the present work to study an important family of strained ring compounds, the [*n*.*m*.0] bicyclic alkanes. The heats of formation *via* oxygen combustion calorimetry of a number of such compounds have been measured in this work to arrive at strain energies.

The heats of formation of this family of hydrocarbons provide an important testing ground for calculation of molecular properties by energy minimization using transferable empirical valence force potential functions. In this work we have also made such calculations for the compounds measured and the other appropriate cycloalkanes for which data exist.

The compounds measured are *cis*-bicyclo[3.1.0]hexane, *cis*-bicyclo[4.1.0]heptane, *cis*-bicyclo[5.1.0]octane, *cis*-bicyclo[6.1.0]nonane, *cis*-bicyclo[4.2.0]octane, *cis*-bicyclo[3.3.0]octane, *trans*-bicyclo[3.3.0]octane, and *cis*-bicyclo[5.3.0]decane.

Experimental Section

Compounds Studied. The four cyclopropane ring containing compounds had been synthesized by the Simmons–Smith reaction[2] and were furnished to us by Dr. Simmons. Bicyclo[4.2.0]-octane was synthesized by us by photolysis of cycloocta-1,3-diene[3] in benzene followed by hydrogenation. *cis*- and *trans*-bicyclo-[3.3.0]octane were synthesized in Professor N. L. Allinger's laboratory at Wayne State University and the details are given in the M.S. Thesis of one of us (M. J. H.).[4] *cis*-Bicyclo[5.3.0]decane was made by hydrogenation (at 1 atm catalyzed by reduced platinum oxide) of a commercial sample of azulene (Aldrich Chemical Co.) that had been purified by sublimation by us. The compounds were either purified by gas–liquid chromatography (glc) or showed no extraneous peaks by glc after distillation.

Heats of Combustion. These were measured with a calorimeter and techniques previously described.[5,6] A G-2 Mueller bridge (Leeds and Northrup 8069-B) was used for the resistance ther-

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[2] H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, 81, 4256 (1959).

[3] W. G. Dauben and R. L. Cargill, *J. Org. Chem.*, 27, 1910 (1962).

[4] M. J. Hickey, M.S. Thesis, Wayne State University, 1969.

[5] R. H. Boyd, R. L. Christensen, and R. Pua, *J. Amer. Chem. Soc.*, 87, 3554 (1965).

[6] R. H. Boyd, K. R. Guha, and R. Wuthrich, *J. Phys. Chem.*, 71, 2187 (1967).

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