was agitated at full power for 1 min. The resulting precipitate was collected by filtration, washed with water, and dried by drawing air through it. The crude peroxide was dissolved in acetone (180 ml), the solution was filtered, and after reduction in volume to 90 ml the filtrate was cooled in Dry Ice. The *p*-nitrobenzenesulfonyl peroxide-*sulfonyl*-^{18}O (4.6 g, 46% yield) which precipitated, after collection on a filter and drying *in vacuo*, melted at 125° (lit.[2] mp 127°).

p-Nitrophenylsulfonoxylation of p-Xylene. *p*-Nitrobenzenesulfonyl peroxide-*sulfonyl*-^{18}O (0.202 g, 0.5 mmol) in ethyl acetate (50 ml) and *p*-xylene (5.3 g, 0.05 mol) was stirred at room temperature for 24 hr. The mixture was washed successively with 5% aqueous potassium hydroxide (25 ml), 5% hydrochloric acid (25 ml), and water (40 ml) and dried with magnesium sulfate, and the solvent was removed *in vacuo*. Recrystallization of the residue from 1:1 benzene–heptane gave *p*-xylyl *p*-nitrobenzenesulfonate (0.083 g, 54%) which had an infrared spectrum identical with that of an authentic sample. This ester was subjected to mass spectral analysis (Table I, expt 1).

p-Nitrophenylsulfonoxylation of Benzene in Methylene Chloride. A mixture of labeled peroxide (3.1 g) in benzene (9.3 g) and methylene chloride (89 ml) was stirred at room temperature for 85 hr. A procedure identical with that above gave phenyl *p*-nitrobenzenesulfonate, mp 114–116° (lit.[15] mp 114°). The infrared spectrum was identical with that of an authentic sample. A portion of this ester, by the procedure given below, was converted to the trimethylsilyl ether, which was subjected to mass spectral analysis (Table I, expt 2).

Reaction of p-Nitrobenzenesulfonyl Peroxide-*sulfonyl*-^{18}O with Benzene in Ethyl Acetate Solution. A solution of *p*-nitrobenzenesulfonyl peroxide-*sulfonyl*-^{18}O (2.6 g, 6.5 mmol) in ethyl acetate (75 ml) and benzene (7.8 g, 0.1 mol) was stirred at room temperature for 70 hr. By a procedure identical with that previously described, phenyl *p*-nitrobenzenesulfonate was isolated and subjected directly to mass spectral analysis (Table I, expt 4).

In a duplicate run this ester was cleaved to phenol, which was converted to the trimethylsilyl ether, which was then analyzed by mass spectrometry. Phenyl *p*-nitrobenzenesulfonate (0.73 g, 2.62 mmol) labeled with oxygen-18 and tetrahydrofuran (10 ml) were placed in a flask fitted with a rubber septum and purged with nitrogen for 5 min. Sodium–naphthalene in tetrahydrofuran[8] (0.6 *M*, 30 ml) was added *via* a syringe and after 3 min of stirring, water (0.5 ml) was added to quench the excess sodium–naphthalene. The mixture was filtered through a fritted glass funnel and the tetrahydrofuran was removed using a rotary evaporator. The residue was dissolved in ether (30 ml) and extracted with three 40-ml portions of 0.1 *M* KOH. The combined alkaline solutions were acidified with 3 *M* HCl and extracted with ether (three 50-ml portions). The combined ether extracts, after drying with magnesium sulfate, were evaporated *in vacuo*. To the residue was added hexamethyldisilazane (5 ml) and a trace of sand, and the mixture was refluxed for 3 hr. Vacuum distillation of the mixture gave a forerun of hexamethyldisilazane and a clear liquid (0.2 ml) whose infrared spectrum was identical with that of an authentic sample of phenyl trimethylsilyl ether. This liquid was subjected to mass spectral analysis (Table I, expt 3).

Reaction of p-Nitrobenzenesulfonyl Peroxide-*sulfonyl*-^{18}O with Benzene (Neat). *p*-Nitrobenzenesulfonyl peroxide-*sulfonyl*-^{18}O (1.0 g, 2.5 mmol) in benzene (50 g, 0.64 mol) was allowed to stand overnight at room temperature. By the procedure already described, phenyl *p*-nitrobenzenesulfonate was isolated and subjected to mass spectral analysis (Table I, expt 5).

Registry No.—*p*-Nitrobenzenesulfonylperoxide, 6209-72-9; *p*-xylene, 106-42-3; benzene, 71-43-2.

References and Notes

(1) (a) Supported in part by the U. S. Army Research Office (Durham) through Grant DA-ARO-(D)-31-124-G720 and by National Science Foundation Grant GP-19018. (b) Taken in part from the dissertation of R. V. Hoffman, submitted to the Graduate School of Case Western Reserve University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Dec 1969. (c) Presented in part at the International Symposium on the Chemistry of Organic Peroxides, Berlin, 1967.
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Reactivity of Aryl Nitrenes. Competition between Carbazole Formation and Internal Bond Reorganization in Biphenylnitrenes

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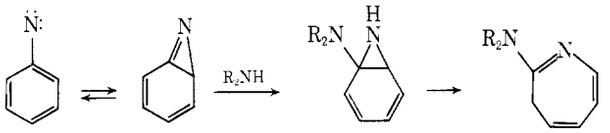
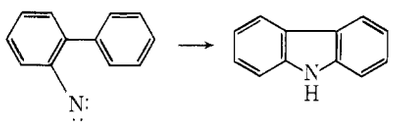
A series of three 3′,5′-disubstituted 2-azidobiphenyls (**1b–d**) has been prepared. The sensitivity of carbazole yield on photolysis to the presence of the nucleophilic trapping agent diethylamine (DEA) has been determined and compared with similar data for the unsubstituted compound **1a**. All four compounds exhibit formation of some 2-diethylamino-3-aryl-3*H*-azepine (**3a–d**) as well as the expected carbazole (**2a–d**) on photolysis in the presence of DEA. For electron-withdrawing substituents (CF_3, CO_2CH_3) the drop in carbazole yield is from ~80 to ~20–30% but for CH_3 and the unsubstituted compound the decrease is somewhat less. Deoxygenations of 2-nitrosobiphenyl and the 3′,5′-bis(trifluoromethyl) analog were studied to provide an alternative source of the presumed nitrene intermediates. These results appear to require revision of previous mechanisms for formation of carbazole from biphenylnitrene to include an azirine intermediate which can be diverted to azepine formation by DEA.

The chemistry of phenylnitrene is dominated by an internal bond reorganization which eventually leads to ring-expanded products in the presence of nucleophilic trapping agents, specifically secondary amines.[1] The initial reaction in this sequence is very rapid and flash-photolysis studies indicate that phenylnitrene has a half-life of 30 μsec or less.[1a] Intermolecular addition and insertion reactions are inefficient processes for phenylnitrene.[2,3] In contrast, arylnitrenes with adjacent sites of unsaturation cyclize with efficiency.[4] Biphenylnitrene, for example, gives carbazole in yields of around 80%.[5] The cause of the general inefficiency of intermolecular reactions of phenylnitrene may lie in the



rapidity of cyclization to the azirine and subsequent decomposition of this intermediate. An alternative view is that unsubstituted arylnitrenes are not as highly electron deficient as necessary to promote typical nitrene reactivity.[6] The two points of view are not mutually exclusive and both factors might contribute to the lack of intermolecular insertion reactions for phenylnitrene. We were interested

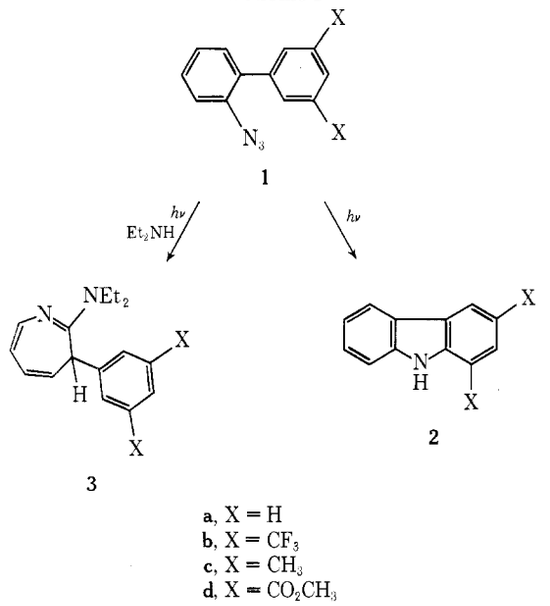


in probing the possibility of competition between the internal bond reorganization process and carbazole formation for biphenylnitrenes. In this paper we report on the generation of such nitrenes in the presence of secondary amines which serve to trap the azirine intermediate formed by internal bond reorganization.

Results

Preliminary experiments involving photolysis of biphenyl azide in THF–DEA mixtures resulted in the formation of 2-diethylamino-3-phenyl-3*H*-azepine and an accompanying decrease in carbazole yield.[7] The deoxygenation of *o*-nitrobiphenyl, which presumably proceeds through the same nitrene intermediate, also gives rise to this azepine.[8] In order to study this competitive trapping process in more detail, a series of substituted biphenyl azides (**1a–d,** Scheme I) was prepared. 3′,5′-Disubstituted systems were

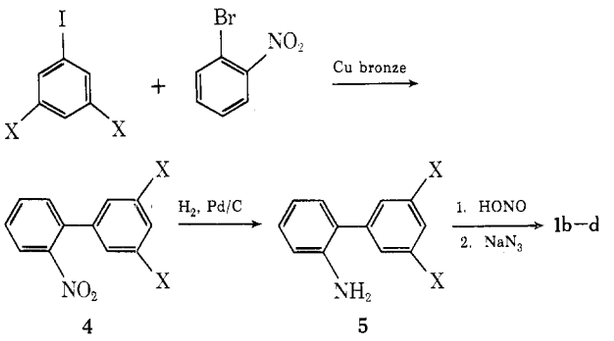
Scheme I



a, X = H
b, X = CF_3
c, X = CH_3
d, X = CO_2CH_3

chosen. The symmetrical substitution results in there being a single possible carbazole product, and the presence of two substituent groups should accentuate any electronic effects on the competition between carbazole and azirine formation. The Ulmann coupling reaction of 3,5-disubstituted iodobenzenes with *o*-bromonitrobenzene proved to be a generally satisfactory synthetic method. Details of the syntheses, which are outlined in Scheme II, are given in the Experimental Section.

Scheme II



Photolyses of **1a, 1b,** and **1c** were carried out in THF–DEA mixtures of varying concentration containing 5% by volume of piperylene.[9] The yield of the appropriate carbazole was measured by glpc in each case. Quantitative yield data were also obtained for the azepine in the case of **1a** and **1b.** The carbazole yield data are summarized in Table I. In each of the systems, it was possible to effect a substantial diversion of the nitrene intermediate from carbazole formation at sufficiently high DEA concentration. The effect is quite dramatic in the case of **1b,** the bis(trifluoromethyl) system. The yield of carbazole **2b** drops from >80 to ~20% as DEA is incorporated into the solvent mixture to the extent of 1% (~0.1 *M*). Further addition of DEA up to and including use of DEA as the solvent medium (along with 5% by volume piperylene) causes no further diminution in carbazole yield.

For **1a** and **1c** the concentration required for maximum diversion from carbazole formation is much higher (~50% or ~5 *M*). The amount of nitrene which cannot be diverted to azepine is also substantially higher for **1a** and **1c,** being 40 ± 10%.

The bis(carbomethoxy) compound **1d** proved to be unsuitable for extensive quantitative study but qualitatively resembled the trifluoromethyl system. The substituted carbazole **2d** was formed in 82% yield in the absence of DEA but dropped to 27 ± 1% in solution containing 5, 95 and 100% DEA. The azepine **3d** was formed in 45 ± 1% yield under these conditions.

Azepine **3a** has been previously described.[7,8,12] The nmr spectra of the substituted analogs **3b–d** were very similar. In addition to the peaks expected for the diethylamino group and the 3-aryl groups, each compound showed a doublet (H-7) and multiplet (H-5) near 6.7–6.8 and 6.3–6.5 ppm, respectively. In each case the other azepine ring protons appear as a multiplet at 5.2–5.4 ppm.

Azepine yield data were measured in the experiments with **1a** and **1b.** These data are included in Table I. It is evident that the drop in carbazole yields is largely accounted for by azepine formation.

The extent of internal bond reorganization as measured by azepine formation has been found to be wavelength dependent for *p*-cyanophenyl azide.[10] With 3500-Å light a hydrazine formed by nucleophilic trapping without bond reorganization is the major product while 2537-Å light leads to the azepine and hydrazine in comparable amounts. We photolyzed **1a** and **1b** with both unfiltered 2537-Å and 3000-Å light filtered through Pyrex. The data for **1a** indicate that a wavelength dependence is present. The azepine: carbazole ratio (Table II) is consistently higher and the azepine yield higher with the 2537-Å source than with the longer wavelength source. The data for **1b** exhibit a similar trend. Control experiments in the unsubstituted system indicated that photodestruction of **3a** was not significant

Table I
Product Yields[a] as a Function of Diethylamine Concentration and Light Source

		1a						1b						1c
		Mixed[c]		2537 Å[d]		>2900 Å[e]		Mixed[f]		2537 Å[g]		>2900 Å[h]		Mixed[i]
% DEA	M^b	2a	3a	2a	3a	2a	3a	2b	3b	2b	3b	2b	3b	2c
0	0	86	0	76	0	76	0	81	0	70	0	—	—	81
0.5	0.49							29	49	26	43	45	41	
1.0	0.98							22	55	19	51	35	44	
2.0	0.20							20	63	16	56	31	47	
3.0	0.29							22	69					
5.0	0.48	73	4	71	8			21	70	15	57			76
10.0	0.98	69	9	58	22	64	4	15	68					62
25.0	2.4	64	25	49	37	56	16	15	68					62
50.0	4.8	62	28	41	45	52	18	17	64					51
75.0	7.3	49	30	39	52	47	22	15	66					41
90.0	8.8	53	33					16	63					39
95.0	9.3	49	33	32	43			17	65					40

[a] Yields quoted are averages of at least two separate runs. In most cases duplicate values were within ±3 percentage units of the mean. Occasional instances of wider deviation were checked with additional runs. [b] Calculated assuming additivity of solvent volume. [c] 30-min photolysis; 40–50% azide decomposition; light source was unfiltered irradiation from Southern New England Ultraviolet RPR 3000-Å lamps. [d] 30-min photolysis; 60–70% azide decomposition; light source was unfiltered irradiation from RPR 2537-Å source. [e] 60-min photolysis; 50–55% azide decomposition; RPR 3000-Å source filtered through Pyrex. [f] 120-min photolysis; 75–85% azide decomposition; unfiltered RPR 3000-Å source. [g] 60-min photolysis; >90% azide decomposition; unfiltered RPR 2537-Å source. [h] 120-min photolysis; 75–80% azide decomposition; RPR 3000-Å source filtered through Pyrex. [i] 60-min photolysis; 65–80% azide decomposition; unfiltered RPR 3000-Å source.

over periods of up to 2 hr under the conditions used in collecting the analytical data. There was some photolysis of carbazole evident in the control experiments but this was more significant with the 3000-Å source and therefore cannot be responsible for the lower azepine:carbazole ratio at the longer wavelength.

Deoxygenation of aromatic nitroso compounds provides an alternative method for generation of arylnitrenes in solution near room temperature.[11] Data for deoxygenation of *o*-nitrosobiphenyl and 2-nitroso-3′,5′-bis(trifluoromethyl)-biphenyl are given in Table III. It is evident that the nitrenes formed by deoxygenation can also be diverted to azepine. The yields in the deoxygenation reactions, however, are lower than in the photolyses. The ratios of these two products are similar for the two alternative sources of the nitrene. Deoxygenation of2-nitroso-3′,5′-bis(trifluor omethyl)biphenyl also results in total azepine and carbazole yields below those obtained in the photolysis. In THF–DEA mixtures, the ratio between azepine and carbazole yields is again similar to those found from the azide. However, in the absence of DEA the **2b** yield is only 47% and some of the azo compound is formed. The possibility of a variety of competing processes in the deoxygenation reaction makes attempts at quantitative comparison of the product ratios with the azide photolysis of dubious value.

Discussion

These trapping experiments permit several qualitative statements to be made about the biphenylnitrene intermediate. (1) The formation of azepines and concomitant decrease in carbazole yield imply that the rate of internal bond reorganization must be competitive with intramolecular cyclization to a carbazole. (2) Since carbazole yields are high in the absence of secondary amine trapping agents, the formation of the azepine precursor cannot be an irreversible process which prevents subsequent carbazole formation.[13] (3) The extent to which the nitrene can be diverted from carbazole formation is a function of the substitution on the second ring, with electron-attracting substituents favoring the formation of azepine in the presence of DEA. (4) A significant substituent effect also appears in the concentration of DEA required to obtain the maximum diversion to azepine. (5) Finally, there is qualitative simi-

Table II
Wavelength Dependence of Azepine:Carbazole Ratio

:2a			3b:2b		
% DEA	2537 Å	>2900 Å	% DEA	2537 Å	>2900 Å
25	0.76	0.29	0.5	1.6	0.91
50	1.1	0.35	1.0	2.7	1.2
75	1.3	0.47	2.0	3.5	1.5

Table III
Yield Data for Deoxygenation Reactions

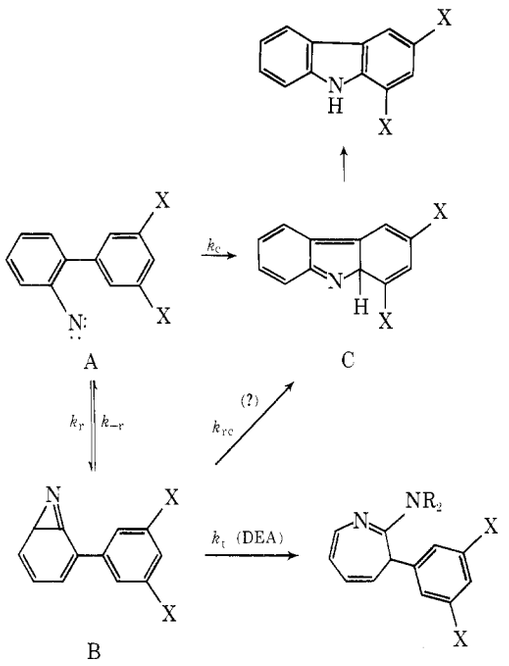
2-Nitrosobiphenyl				2-Nitroso-3′,5′-bis(trifluoromethyl)-biphenyl			
% DEA	2a	3a	3a:2a	% DEA	2b	3b	3b:2b
0	67	0		0	47	0	
25	24	15	0.62	0.5	14	32	2.3
50	23	17	0.74	1.0	13	40	3.1
75	12	11	0.92	5.0	12	48	4.0
100	10	10	1.0	50	13	51	3.9

larity between the behavior of biphenylnitrenes generated by deoxygenation and those generated by azide photolysis. Further discussion of these points will be made with reference to a mechanism similar to that proposed in ref 7 and outlined in Scheme III.

We assume that in the high DEA concentration limit the azepine:carbazole yield ratio reflects primarily k_r:k_c. The existence of a fraction of nitrene which cannot be diverted from carbazole then reflects the competition between the cyclization (k_c) and reorganization (k_r) processes. These are seen to be closely balanced in each of the cases studied with $k_r \lesssim k_c$ for **1a** and **1c** but with $k_r \lesssim 4k_c$ for **1b**. This shift in the case of **1b** is in a reasonable direction if the nitrene attack on the adjacent aromatic ring is viewed as being electrophilic in character and therefore impeded by electron-withdrawing substituents. It is possible that k_c represents the sum of two processes. For example, if both singlet and triplet nitrene are generated, as has been observed in other azide photolyses,[14] k_c would represent the composite of the two independent cyclization processes.

The internal bond reorganization process designated by k_r must either be reversible or there must be a route from the azirine intermediate B to carbazole (such a process is

Scheme III



designated by k_{rc} in Scheme III). These conditions are necessary in order to account for the high yield of carbazole in the absence of nucleophilic trapping agent. A direct rearrangement of the azirine B to carbazole precursor C has some analogy in the facile formation of 2-phenylpyrrole from 3-styrylazirine below room temperature.[15]

We have estimates of some of the rates of the reactions in this scheme from ongoing flash-photolysis studies.[1a,16] Work with phenylnitrene indicates that azirine formation is very rapid.[1a] Reactions of the azirines from *o*-alkylphenylnitrenes with amines are in the range 3×10^4 to 8×10^8 l. mol^{-1} sec^{-1} and a rough rate of $\sim 10^6$ l. mol^{-1} sec^{-1} has been measured for formation of azepine **3b**.[1a,16] Rates of carbazole formation have been reported[17] for **1a** (1.1×10^3 at 292°K) and measured[16] for **1b** ($\sim 1.0 \times 10^2$ at 293°K). These rates permit placing some limits on the pathways for azepine and carbazole formation. In the case of **1b**, 0.1 *M* DEA is sufficient to cause maximal carbazole diversion. The trapping of B at this DEA concentration would be occurring at a rate of $\sim 10^5$ sec^{-1}, much faster than carbazole is formed in the absence of DEA. This indicates the existence of two intermediates, one of which cannot be intercepted by DEA. The nondivertable pathway must account for about 20% of the photolyzed azide. The case of **1a** is more uncertain because it is not possible to measure k_t. We estimate that it would be in the range 10^5–10^4 l. mol^{-1} sec^{-1} on the basis of the value for **1b** and the fact that a substantial electronic effect has been noted in this reaction.[1a] Maximal diversion from carbazole in this case requires 5 *M* DEA; so the rate of azepine formation would be $\sim 5 \times 10^5$ to 5×10^4 sec^{-1} in the high DEA concentration range. This is also sufficiently rapid that carbazole formation ($k \approx 1 \times 10^3$ sec^{-1}) would be completely suppressed if a single carbazole precursor which could be diverted to azepine were involved. Analysis in the case of both **1a** and **1b** appears to require formation *of two intermediates* during or very rapidly after the photolysis step. One of these intermediates can be trapped by DEA; the other cannot. The carbazole yield data indicate that the ratio of trappable to nontrappable intermediate is ~1:1 for **1a** and ~4:1 for **1b**. Although there is much less quantitative data on which to rely, it appears that the distribution of intermediates from **1c** is very similar to that from **1a** whereas **1d** resembles the **1b** case.

The maximum formation of azepine occurs at much lower amine concentrations for **1b** and **1d** than for **1a** and **1c**. This can be attributed to the electronic effect on k_t. With k_t large for **1b** (and, presumably, **1d**) the trapping process is able to divert all the azirine at significantly lower DEA concentration. At this stage the competition is with the processes governed by rate constants k_{-r} and/or k_{rc}.

The data from the nitrosobiphenyl deoxygenations seem to imply the existence of both a trappable and a nontrappable carbazole precursor in this system as well. The yields in the deoxygenation reactions are lower and the likely involvement of other reactions which consume nitroso compound, nitrene intermediate, and probably azepine prevent detailed quantitative comparison of the data from the two sources. However, for both 2-nitrosobiphenyl and the bis(trifluoromethyl) derivative some carbazole formation occurs at high DEA concentrations. The limiting ratios of azepine to carbazole in these two systems (~1:1 and ~4:1, respectively) are roughly similar to those noted in the azide photolysis experiments.

There appears to be some wavelength dependence on the azepine:carbazole ratio. These data are summarized in Table III. The tendency toward diminishing azepine yield at longer wavelength parallels the observation of Odum and Wolf[10] using *p*-cyanophenyl azide. The wavelength dependence of the azepine:carbazole ratio implies that partitioning between the trappable and nontrappable intermediates is affected by the energy of the exciting light. Shorter wavelengths irradiation increases the fraction converted to the trappable intermediate.

There have been several prior studies on the mechanism of formation of carbazole after photolysis of *o*-biphenyl azide. Reiser and coworkers examined the reaction in an EPA glass at 77°K. They observed formation of an intermediate which was converted to carbazole by subsequent irradiation.[18] The interpretation was that the intermediate was triplet *o*-biphenylnitrene. Cyclization, which was implied to involve hydrogen abstraction and recombination, was considered to proceed through excitation of the triplet intermediate. A singlet-state species as the reactive intermediate was not considered to have been excluded. Later, this group examined carbazole formation in a polymer matrix at room temperature.[19] Flash photolysis generated an intermediate which decayed at a rate of ~350 sec^{-1} and was considered to be triplet *o*-biphenylnitrene. The rate constant was associated with cyclization to carbazole and was considered to involve intramolecular hydrogen abstraction followed by rapid recombination to give carbazole. Swenton, Ikeler, and Williams[5b] studied the photolysis in benzene near room temperature in the presence of various sensitizers and quenchers. Their results appeared most consistent with a singlet nitrene intermediate but the multiplicity was considered an open question. Lehman and Berry[17] measured the rate of carbazole appearance from a photochemically generated intermediate between 5 and 46° in cyclohexane. The rate constant at 24° is 1.85×10^3 sec^{-1}. They concluded that the rate-determining step is intramolecular addition of triplet *o*-biphenylnitrene to the adjacent aromatic ring, generating a diradical which rapidly goes to carbazole by hydrogen atom migration. The absorption spectrum of the transient species, which is the same as that observed by Reiser,[18,19] was the principal basis for identifying the intermediate as the triplet nitrene.

None of these mechanisms consider the possibility of a reversible intramolecular bond reorganization process. In fact, these mechanisms make it very difficult to account for

the formation of azepines. The species being trapped cannot be singlet biphenylnitrene, since it would not be expected to have sufficient lifetime to permit reaction with DEA to occur over the period of 0.01–1.0 msec during which the trapping reaction occurs.[1a] An addition reaction of triplet biphenylnitrene with DEA is not readily visualized. Neither is a mechanism for formation of the azepine initiated by a hydrogen-abstraction step attractive. The evidence against hydrogen-abstraction processes includes the fact that negligible amounts of *o*-biphenylamines are formed in these reactions. Our data indicate that photodecomposition of biphenyl azides generates two reactive intermediates, only one of which can be diverted by DEA.

We suggest that the trappable carbazole precursor is the azirine B. This type of structure is generally assumed[1b,13] to be the precursor of azepines in aryl azide thermal and photochemical decompositions. Our data do not permit a conclusion on the question of the route of conversion of B to carbazole. This could occur *via* the nitrene A by reversal of the cyclization step or by way of a carbazole precursor such as C.

The assignment of a structure to the nontrappable intermediate is more uncertain. The nontrappable carbazole precursor could be C. If it were irreversibly formed competitively with B, a route to carbazole insensitive to trapping by DEA would exist. If k_{-r} and/or k_{rc} were large relative to conversion of C to carbazole, the concentration of C would rapidly build up. This mechanism would then attribute structure C to the carbazole precursor which has been observed by Reiser and coworkers[18,19] and by Berry and Lehman.[17] Although in contradiction to previous assignments of this intermediate as the triplet nitrene, it should be pointed out that the previous spectral assignments[20] rest on similarity of the spectrum to those of other triplet aryl nitrenes and have not, for example, been corroborated by esr measurements. So far as we have been able to determine there are no recorded spectra of the 8a*H*-carbazole chromophore present in C; so it is an open question as to whether the observed spectrum is compatible with structure C.

Alternatively, the nontrappable intermediate could be considered to be the triplet form of the nitrene, ^{3}A. It would be expected that ^{3}A would not be converted to azirine B and therefore would not be diverted by DEA. Formation of triplet nitrene in photolytic azide decompositions has adequate precedent.[14] Since this is the ground state of the nitrene, ^{3}A could be formed from B by reversal to singlet nitrene followed by spin inversion. In this way B could be converted to ^{3}A and then to carbazole in the absence of DEA. A reservation to assigning ^{3}A as the nontrappable carbazole precursor is the fact that this assignment requires that the triplet nitrene be rather long lived ($t_{1/2}$ for conversion to carbazole ~1 msec) even in the presence of a substantial (0.01 *M*) concentration of piperylene.[16]

The present data do not seem to permit an unambiguous assignment of structure to the nontrappable carbazole precursor but do require that previously postulated mechanisms be modified to account for the ability of DEA to divert some of the nitrene to azepine.

Experimental Section[21]

3′,5′-Bis(trifluoromethyl)-2-nitrobiphenyl (4b). A stirred mixture of 3,5-di(trifluoromethyl)iodobenzene[22] (34.0 g) and 1-bromo-2-nitrobenzene (20.2 g) was heated to 180°. Copper bronze (15 g) was added in portions over 0.5 hr and heating was continued for 3 hr after the addition was complete. The cooled reaction mixture was extracted with hot chloroform and after filtration and concentration the residue was chromatographed on alumina. Ether–hexane (1:4) eluted **4b** and it was recrystallized from ethanol (10.1 g, 30%): mp 76.5–77°; nmr ($CDCl_3$) δ 7.80 (m); mass spectrum *m/e* (rel intensity) 335 (27), 315 (30), 285 (58), 270 (20), 269 (100), 266 (18), 238 (32), 237 (17), 236 (28), 220 (54), 219 (54), 201 (27), 199 (16), 170 (20), 169 (16), 75 (15).

2-Amino-3′,5′-bis(trifluoromethyl)biphenyl (5b). Reduction of **4b** in ethanol over Pd/C proceeded quantitatively to give **5b,** which was recrystallized from hexane, mp 44–45°.

2-Azido-3′,5′-bis(trifluoromethyl)biphenyl (1b). Procedure A of Smith and Brown[23] was used. An ether extract of the azide was washed with dilute HCl, 5% $NaHCO_3$, and water. Drying and evaporation of the ether gave **1b** as a white solid which was recrystallized from 95% ethanol: mp 43–43.5°; nmr ($CDCl_3$) δ 7.29 (4, m), 7.84 (3, s); mass spectrum *m/e* (rel intensity) 331 (2), 303 (24), 284 (32), 283 (100), 234 (48), 233 (19), 214 (17), 213 (17), 75 (19), 69 (46).

3,5-Dimethyliodobenzene. 3,5-Dimethylaniline (5.0 g) was dissolved in 65 ml of 25% sulfuric acid and the solution was cooled to −10°. Aqueous $NaNO_2$ was added until starch–iodide paper indicated the presence of unreacted nitrous acid. A solution of KI (8.0 g) was then added, keeping the reaction mixture below 0°. The solution was kept overnight at room temperature, warmed for 0.5 hr on a steam bath, and finally extracted with ether. Distillation gave the product, bp 51–53 (1 mm), in 52% yield, nmr ($CDCl_3$) δ 2.23 (6, s), 6.90 (1, s), 7.30 (2, s).

2-Amino-3′,5′-dimethylbiphenyl (5c). A mixture of 3,5-dimethyliodobenzene (12.3 g) and 1-bromo-2-nitrobenzene (10.0 g) was heated to 170–180° with stirring and copper bronze (10.0 g) was added in small portions over 30 min. The solution was then maintained at 180° for 3 hr. The reaction mixture was extracted with boiling chloroform, filtered, concentrated, and distilled. After some unreacted iodo compound was recovered, **4c** (6.9 g, 57%) distilled at 130–135° (0.5 mm). Reduction over Pd/C in ethanol for 3 hr at 3 atm hydrogen gave **5c** in quantitative yield after distillation, nmr ($CDCl_3$) δ 2.30 (6, s), 3.7 (2, s), 6.85 (7, m).

2-Azido-3′,5′-dimethylbiphenyl (1c). The azide was prepared following procedure A of Smith and Brown.[23] The crude azide was extracted with ether and washed successively with 2 *N* hydrochloric acid, 5% $NaHCO_3$ solution, and water. After drying and evaporation of the solvent, the residual oil was purified by elution through silica gel with benzene. Evaporation of the benzene left an oil which was pure **1c** as judged by glpc, tlc, and spectral data. The compound decomposed on attempted distillation and no satisfactory analysis was obtained.

Dimethyl 5-Iodoisophthalate. 5-Iodoisophthalic acid was prepared according to the procedure of Grahl[24] and then esterified. The product was recrystallized from 95% ethanol, mp 100–102° (lit.[25] mp 104–105°).

3′,5′-Dicarbomethoxy-2-nitrobiphenyl (4d). The coupling reaction was carried out as for **4b** but the heating period was reduced to 2 hr. Chromatography on alumina using 1:9 ether–benzene gave **4d** (44% yield) which was recrystallized from benzene–hexane: mp 145–147°; nmr ($CDCl_3$) δ 3.92 (6, s), 7.45 (4, m), 8.15 (2, d, J = 1.5 Hz), 8.68 (1, m).

2-Amino-3′,5′-dicarbomethoxybiphenyl (5d). Reduction over Pd/C at 3 atm pressure in 1:1 ethanol–tetrahydrofuran gave **5d** (88% yield): mp 129–131° after recrystallization from 95% ethanol; nmr ($CDCl_3$) δ 3.92 (8, s overlapping exchangeable NH_2 signal), 7.00 (4, m), 8.30 (2, m), and 8.60 (1, m).

2-Azido-3′,5′-dicarbomethoxybiphenyl (1d). The procedure described for **1b** gave **1d** in 71% yield: mp 103–104° after recrystallization from 95% ethanol; nmr ($CDCl_3$) δ 3.92 (6, s), 7.24 (4, m), 8.22 (2, d), 8.60 (1, t).

Preparation of 1,3-Disubstituted Carbazoles. Samples of each of the carbazoles **1b–d** were prepared by thermolysis of the appropriate azides in decalin at 170–190° for 0.5–1.5 hr.

A. 1,3-Bis(trifluoromethyl)carbazole (2b). Chromatography of the pyrolysis solution gave **2b** (eluted by petroleum ether) in quantitative yield: mp 109–111° after recrystallization from benzene; uv (95% ethanol) λ_{max} (log ϵ) 215 (4.59), 241 (4.48), 267 (4.49), 300 (3.96), 331 nm (3.60); nmr (acetone-d_6) δ 7.48 (3, m), 7.92 (1, s), 8.27 (1, d, J = 7 Hz), 8.70 (1, s), 11.1 (1, broad).

B. 1,3-Dimethylcarbazole (2c). After elution from alumina with benzene, recrystallization from Skellysolve gave **2c:** mp 93–95° (lit.[26] mp 95°); uv (95% ethanol) λ_{max} (log ϵ) 227 (4.52), 235 (4.58), 240 (4.63), 250 (4.40), 261 (4.26), 297 (4.23), 331 nm (3.60).

C. 1,3-Dicarbomethoxycarbazole (2d). The carbazole (55% yield) precipitated on cooling the pyrolysis solution to −10° and was recrystallized from methanol, mp 193–193.5°.

Preparation and Characterization of 3-Aryl-2-diethylamino-3*H*-azepines. A. 2-Diethylamino-3-phenyl-3*H*-azepine (3a). This compound has been previously described.[7,8] A sample

Table IV
Control Data[a]

Photolysis time, hr	Yield, %: 2537 Å 2b	2537 Å 3b	>2900 Å 2b	>2900 Å 3b
0.5	52	39	67	15
1.0	44	40	60	15
2.0	45	37	54	18
4.0			48	17

[a] Photolyses were carried out in 25% DEA.

obtained in the present work by photolysis of **1a** in DEA had spectral properties identical with those of the material prepared during the previous work.[7]

B. 2-Diethylamino-3-[3,5-bis(trifluoromethyl)phenyl]-3*H*-azepine (3b). A solution of **1b** (451 mg) in 30 ml of 95:5 DEA–piperylene was deoxygenated by a nitrogen stream and photolyzed for 2.5 hr in a series of quartz test tubes using 3000-Å lights in a Rayonet Model RS photochemical reactor. After photolysis each tube was treated with 5 ml of 1% acetic acid in methanol and allowed to stand overnight to ensure completion of tautomerism to the stable 3*H* isomer.[1b] The solvent was evaporated and the residue was chromatographed on alumina. Ether–hexane containing ~2% methanol eluted the azepine (155 mg, 30%). Further purification by preparative glpc on a 6-ft, 5% FS1265 column at an oven temperature of 170° gave a light yellow oil: $\nu_{C=N,C=C}$ 1560, 1520 cm^{-1}; nmr ($CDCl_3$) δ 2.20 (6, t), 3.46 (4, q), 5.40 (3, m), 6.55, (2, d superimposed on m), 7.52 (3, s).

2-Diethylamino-3-(3,5-dimethylphenyl)-3*H*-azepine (3c). A solution of **1c** (520 mg) in 40 ml of 95:5 DEA–piperylene was photolyzed and processed as described for **3b.** Chromatography gave 248 mg of unreacted **1c** and some of the carbazole **2c** (90 mg, 38%). Ether–hexane containing about 2% methanol eluted **3c** (96 mg, 29%) which was further purified by preparative glpc under the same conditions as for **3b:** $\nu_{C=N,C=C}$ 1570, 1530 cm^{-1}; nmr ($CDCl_3$) δ 1.18 (6, t), 2.18 (6, s), 3.45 (4, q), 5.42 (3, m), 6.7 (5, m).

3-(3,5-Dicarbomethoxyphenyl)-2-diethylamino-3*H*-azepine (3d). A solution of **1d** (232 mg) in 20 ml of 95:5 DEA–piperylene was photolyzed for 2 hr and then worked up as described for **3b.** Addition of ether to the residue from evaporation of solvent resulted in the precipitation of **3d** (25% yield), which was recrystallized from petroleum ether: mp 171–172°; $\nu_{C=N,C=C}$ 1570, 1520 cm^{-1}; nmr ($CDCl_3$) δ 1.20 (6, s), 3.52 (4, q), 3.88 (6, s), 5.40 (3, m), 6.64 (d, superimposed on m), 7.92 (2, s, slightly broadened), 8.35 (1, s, slightly broadened).

Conditions for Photolysis and Quantitative Product Analysis. Accurately weighed amounts (~50 mg) of the azide were placed in quartz test tubes and dissolved in the appropriate solvent mixture. Solvent mixtures were prepared volumetrically by adding 0.50 ml of piperylene and the appropriate amount of DEA to a volumetric flask and then diluting to 10 ml with THF. An aliquot (5.0 ± 0.2 ml) of the solution was then transferred to the test tubes, which were capped with rubber septa and deoxygenated with nitrogen for about 5 min using a hypodermic needle. The tubes were then placed in a merry-go-round apparatus centered in a Rayonet Type RS reactor and photolyzed at 38°.[27] Photolysis times are included in Table I. At the completion of the photolysis 5 ml of 1% acetic acid in methanol was injected into each test tube. The tubes were kept capped overnight at room temperature. The appropriate internal standard was added and analysis for unreacted azide, carbazole, and azepine (except for **3c**) was then carried out under the following conditions: **1a, 2a,** and **3a,** 5% OV-101 column, isothermal at 160° with stilbene internal standard; **1b, 2b,** and **3b,** 5% SE-30 column, 140° until the azide elutes then to 180° at 8°/min with carbazole internal standard; **1c** and **2c,** 5% FS1265, temperature programmed over 140 to 190° at 10°/min beginning at injection with carbazole internal standard. Detection was by flame ionization on Varian Aerograph Model 1800 or 2440 gas chromatographs.

Analysis of the reaction mixtures from **1d** were carried out by evaporating the solvent and dissolving the residue in methylene chloride. The azepine **3d** was extracted by 6 *N* HCl. After neutralization with 8 *N* NaOH the azepine was extracted into methylene chloride and diluted volumetrically. The azepine yield was determined by uv absorbance at 291 nm. The carbazole yield was determined by uv absorbance at 358 nm in the original methylene chloride solution. The yields were corrected for unreacted azide by recovery of the azide by chromatography.

Control Experiments to Determine Product Stability (Table IV). Selected reaction solutions were photolyzed for periods longer than reported in Table I to determine product photosensitivity. Secondary photolysis of the product during the photolysis times used in the analytical experiments was significant only for carbazole.

2-Nitrosobiphenyl (6a). The procedure of Havinga and coworkers[28] was used. After recrystallization from ethanol the compound melted at 112–114°, somewhat higher than previously reported (lit.[11a,28] mp 101°). The nmr was concentration dependent because of dimerization of **6a.** A doublet at δ 5.82 is due to dimer while that at δ 6.16 is due to monomer. Approximate ratios at several molarities in $CDCl_3$ follow: 1.0 *M* 1:1; 0.5 *M*, 2:1; 0.25 *M*, 3:1; 0.13 *M*, large. These ratios indicate that *K* for dimerization = 1.7 ± 0.3 mol^{-1}.

3′,5′-Bis(trifluoromethyl)-2-nitrosobiphenyl (6b). A solution of the amine **5b** (500 mg) in 20 ml of dichloromethane was treated dropwise with *m*-chloroperoxybenzoic acid (0.6 g) dissolved in 20 ml of dichloromethane. The solution was allowed to stir at 0° overnight, warmed to room temperature, and washed several times with 5% $NaHCO_3$ solution. The solution was then dried and evaporated. The residue was dissolved in toluene and eluted through a small alumina column with toluene. The solvent was evaporated at reduced pressure and the residue was recrystallized from ether–benzene to give **6b,** mp 123–124°.

Deoxygenation Reactions. A. Nitrosobiphenyl. A weighed solution of the nitroso compound (~50 mg) in THF (1 ml) was added over a period of 15 min to 20 ml of a cold (−10°) solution of the appropriate THF–DEA mixture containing 0.3 ml of triethyl phosphite. The solution was then kept at room temperature for several hours and then the solvent was removed. Triethyl phosphite was removed using a vacuum pump and the residue was analyzed by glpc.

B. 2-Nitroso-3′,5′-bis(trifluoromethyl)biphenyl. The procedure was identical with that used for nitrosobiphenyl except that the reaction was run at 38°. After removal of the solvent, glpc analysis was carried out. Runs on a 200-mg scale indicated some 2,2′-bis(3,5-trifluoromethylphenyl)azobenzene (**7b**) to be formed (~10%) both in the presence and absence of DEA in addition to **2b** and **3b.**

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Registry No.—**1a,** 7599-23-7; **1b,** 51839-01-1; **1c,** 51839-02-2; **1d,** 51888-57-4; **2a,** 86-74-8; **2b,** 51839-03-3; **2c,** 18992-68-2; **2d,** 51839-04-4; **3a,** 24955-75-7; **3b,** 51839-05-5; **3c,** 51839-06-6; **3d,** 51839-07-7; **4b,** 51839-08-8; **4c,** 51839-09-9; **4d,** 51839-10-2; **5b,** 51839-11-3; **5c,** 51839-12-4; **5d,** 51839-13-5; **6a,** 21711-71-7; **6b,** 51839-14-6; 3′,5′-bis(trifluoromethyl)-2-nitrobiphenyl, 328-73-4; 1-bromo-2-nitrobenzene, 577-19-5; 3,5-dimethyliodobenzene, 22445-41-6; 3,5-dimethylaniline, 108-69-0; dimethyl 5-iodoisophthalate, 51839-15-7; 5-iodoisophthalic acid, 51839-16-8.

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Mechanism of Cycloaddition of Nitroso Compounds with Diphenylketene

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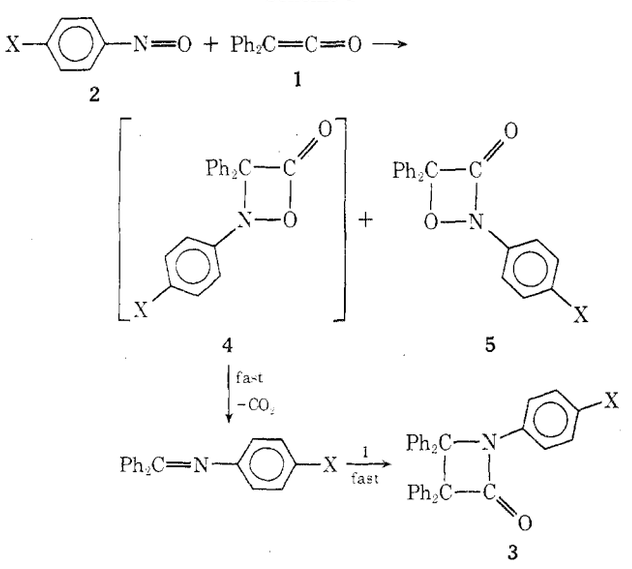
The cycloaddition of aromatic nitroso compounds *p*-X-C_6H_4NO with diphenylketene occurs in all cases rapidly and with relatively low regioselectivity, which is little affected by solvents or substituents. With X = CH_3O, CH_3, H, and CH_3O_2C, the principal product is the 2-aryl-4,4-diphenyl-1,2-oxazetidin-3-one. The isomeric oxazetidin-4-one, the main primary product for X = $(CH_3)_2N$, is unstable in all cases and decomposes to carbon dioxide and a Schiff base, which reacts *in situ* to form an azetidinone. The oxazetidin-3-ones undergo a very facile solvolysis reaction, apparently *via* a nitrenium ion-like intermediate. The cycloaddition results suggest a near-concerted mechanism.

Like most reactions of ketenes, the cycloaddition with nitroso compounds was discovered by Staudinger, who reported in 1911[1] that diphenylketene (**1**) reacted with *p*-dimethylaminonitrosobenzene (**2a**) to yield ultimately the β-lactam **3a** (65%). Staudinger proposed that **3a** arose *via* an unstable oxazetidin-4-one, **4a,** which decomposed to a Schiff base; the latter was shown to give the product **3a** (Scheme I). In contrast to **2a,** nitrosobenzene (**2b**) gave the oxazetidin-3-one **5b** in 63% yield.[1]

Scheme I



a, X = NMe_2
b, X = H
c, X = OMe
d, X = Me
e, X = CO_2Me
f, X = Br
g, X = Cl

These results were extended by Kresze and Trede,[2] who obtained oxazetidin-3-ones **5d, 5f,** and **5g** in 19–48% yields from **2d, 2f,** and **2g,** and the β-lactam **3c** (40%) from reaction of **2c** with **1.** These workers deduced from the effect of the dimethylamino and methoxy groups on the products that the unstable **4** was produced by a dipolar mechanism and **5** by a concerted process.

Mechanisms of ketene cycloadditions have received substantial theoretical[3-5] and experimental study in recent years. Alkenes,[6-10] vinyl ethers,[11,12] and azo compounds[13-15] react with ketenes by essentially concerted [$_\pi2_s + _\pi2_a$] mechanisms, whereas enamines (at least in part),[16-18] imines,[19-21] carbodiimides,[22] and sulfodiimides[23] react *via* dipolar intermediates.

In contrast to these extensive studies on ketene cycloadditions, nitroso compound cycloadditions have been relatively little studied. Nitroso compounds function as dienophiles in Diels–Alder reactions,[24,25] but their involvement in [2 + 2] cycloadditions, despite a number of erroneous early reports,[26-31] is fairly rare. They do yield [2 + 2] adducts (oxazetidines) with highly halogenated[32,33] and methoxylated[34] alkenes, presumably by diradical processes. More recently, the [2 + 2] cycloaddition of nitroso compounds with ketenimines has been reported and studied by Barker.[35] We report here a study of the mechanism of cycloaddition of diphenylketene (**1**) with substituted nitrosobenzenes, **2.**

Results

The principal tool used in this investigation has been the regioselectivity of the cycloaddition, as affected by substituents and solvents. Previous investigators[1,2] had generally reported the formation of *either* **4** *or* **5** from a given nitrosobenzene derivative, which might be taken to imply a completely regiospecific cycloaddition, had the material balances been better.

In our study, the reaction was run by titrating a solution of **1** with a solution of **2** until the end point was indicated by persistent blue or green color of **2** and the complete disappearance of ketene absorption at 2090 cm^{-1} in the ir. (This procedure was made practical by the great speed of the reaction.) In some cases (X = H, CO_2Me) the primary product **5** was stable and was isolated as such; in