

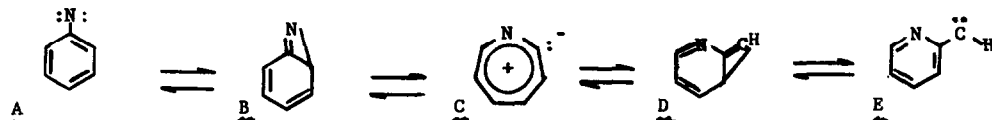
REACTIONS OF ARYL NITRENES. BOND REORGANIZATIONS
IN o-BIPHENYLNITRENE AND PHENYLNITRENE

Richard J. Sundberg, Martin Brenner, Stuart R. Suter and Bijan P. Das

Department of Chemistry, University of Virginia, Charlottesville, Virginia

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Unlike many other types of carbenes and nitrenes, singlet aryl nitrenes have only rarely been observed to undergo intermolecular insertion or addition reactions.¹ It has been suggested^{2,3} that singlet phenylnitrene (A) undergoes intramolecular bond reorganization to a species usually represented as B² but which may be in equilibrium with C, D, and E at least at high temperatures.^{3b} We report here the results of a study aimed at determining if such bond reorganizations are competitive with intramolecular reactions of aryl nitrenes.



We have studied the photolysis of o-biphenylazide (1) and phenyl azide (2) in tetrahydrofuran (THF) containing varying amounts of diethylamine (DEA), an effective reagent for converting B to 2-diethylamino-3H-azepine.^{1b,2} Photolyses were carried out after nitrogen purge in Pyrex test tubes with solutions of 0.8-1.0 mmole of azide in 20 ml of solvent. The reaction mixtures were analyzed by gas chromatography using the internal standard technique. Yields of 3-phenyl-2-diethylamino-3H-azepine (3),⁴ 3-phenyl-2-diethylamino-5H-azepine (4),⁴ carbazole (5) and o-biphenylamine (6) from 1 and of 2-diethylamino-3H-azepine (7) and aniline (8) from 2 are reported as a function of solvent composition in Table I.

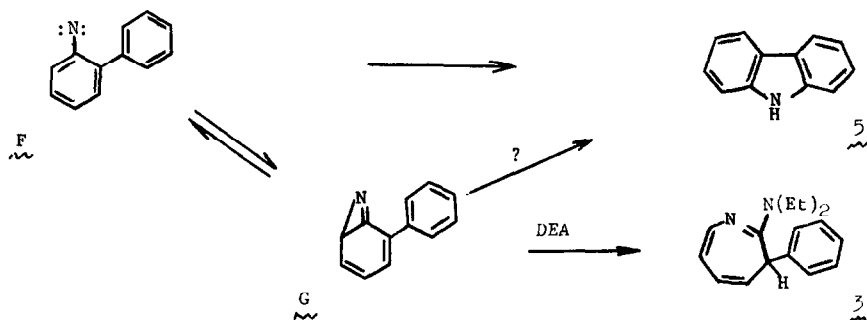
It is clear that o-biphenylnitrene can be partially diverted from carbazole formation by DEA.⁵ The efficiency of the diversion process is a function of DEA concentration. In contrast, the efficiency of conversion of phenylnitrene to 7 is essentially independent of DEA concentration over the range 2-100% DEA. Hydrogen abstraction by biphenylnitrene to give o-aminobiphenyl accounts for very little of the decomposed azide. The same is true for phenylnitrene, except in pure THF where appreciable aniline is formed. We conclude from these results that o-biphenylnitrene undergoes bond reorganization competitively with intramolecular cyclization to carbazole.

Table I. Product Composition

%DEA ^a	Percent Unreacted	Percent Yields ^b					Percent Unreacted	Percent Yields ^c	
		1 <small>mm</small>	3 <small>mm</small>	4 <small>mm</small>	5 <small>mm</small>	6 <small>mm</small>		2 <small>mm</small>	7 <small>mm</small>
0	10	0	0	72	2		48	0	18
2	--	-	-	--	-		55	74	<3
5	19	2	?	56	4		58	73	<3
10	35	10	1	49	5		60	72	<3
25	38	16	1	32	4		60	70	<3
50	43	27	3	25	5		63	66	<3
75	--	--	-	--	-		63	66	<3
100	40	28	4	22	4		63	70	<3

a) In THF by volume b) Based on reacted azide for 0.5 hr photolysis of 0.05 M solution of 1. Reproducibility was satisfactory except for 3, which appeared to decompose at variable rates after termination of the photolysis, although it appears to be stable when neat. Acceptable reproducibility was obtained when analyses were completed within .5hr after termination of photolysis. The recorded yields are averages of at least two runs having maximum absolute deviations of $\pm 3\%$ for 3 and $\pm 5\%$ for 5. c) Based on reacted azide for 1.0 hr photolysis of 0.04 M solution of 2. No problems of reproducibility were encountered.

Previous discussions^{6,7} of the properties of biphenylnitrene have not considered the possibility of competitive bond reorganization. The fact that the extent of diversion of biphenylnitrene is a function of DEA concentration, indicates that the bond reorganization process is reversible. A constant yield of carbazole, independent of DEA concentration, would be expected if bond reorganization and cyclization were competing, irreversible processes.



Reversibility is not, however, a unique explanation for the concentration dependence. A mechanism which includes the transformation $G \rightarrow 5^{\ominus}$ would also predict that the yield of carbazole would be dependent on DEA concentration. Reversibility of bond reorganization could account for the increase in yield of aniline when 2 is photolyzed in pure THF. In the presence of DEA, rapid formation of B, coupled with efficient trapping, can prevent conversion of A to the triplet state. In the absence of DEA, reversal of the bond reorganization step could lead eventually to the triplet nitrene and formation of aniline by hydrogen abstraction. Our data established that bond reorganization of o-biphenylnitrene is competitive with cyclization to carbazole and lend support to the proposal advanced by Abramovitch and Davis⁹ that such bond reorganizations are reversible processes.

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- Cadogan and Todd^{2c} have reported formation of 3 from deoxygenation of o-nitrobiphenyl with diethyl methylphosphonite in DEA. Our sample of 3, collected by preparative glpc showed molecular weight 240.1626 (calc 240.1622), $\lambda_{\max}^{95\% \text{ EtOH}}$ 304 nm (log ϵ 3.93); nmr (δ in CCl_4): 1.17 (t, 6H),

3.42 (q, 4H), 5.2-5.5 (m, 3H), 6.2-6.4 (m, 1H), 6.58 (d, 1H), 6.98 (s, 5H) in agreement with their data. The minor azepine 4 shows molecular weight 240; $\lambda_{\text{max}}^{95\% \text{ EtOH}}$ 236, 300 sh; nmr (δ in CCl_4): 0.9 (t, 6H), 1.8-2.1 (m, 1H), 2.3-2.5 (m, 1H), 2.9-3.6 (m, 4H), 4.6-5.0 (m, 1H), 5.86 (t, 1H), 6.62 (d, 1H), 7.15 (s, 5H).

5. The diversion by DEA appears to be more complete than that observed by Cadogan and Todd in their deoxygenation reaction (10% 3, 67% 5 in 90% DEA). However, the formation of carbazole in this deoxygenation may not proceed exclusively via o-biphenylnitrene; J. I. G. Cadogan and A. Cooper, J. Chem. Soc., B, 883 (1969).
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8. Although without direct precedence, the transformation G \rightarrow 5 is somewhat similar to the conversion of 2-methyl-3-phenylazirine to 2-methylindole: K. Isomura, S. Kobayashi and H. Taniguchi, Tetrahedron Lett., 3499 (1968). Boyer^{ad} has also suggested the possibility of carbazole formation after bond reorganization of o-biphenylnitrene.
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