

moist ether. The precipitated alumina was removed and the solvent evaporated under reduced pressure. The residue, on recrystallization from alcohol, yielded 35 mg. of tan crystals, m.p. 168–170°. The composition and molecular weight of this product would indicate that it is the result of hydrogenolysis of peroxide linkages.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 79.97; H, 6.71; mol. wt., 240. Found: C, 80.54; H, 6.96; mol. wt. (Rast), 262.

Catalytic hydrogenation of the black crystals gave a similar result. A mixture of 90 mg. of the black crystals,

25 mg. of prerduced Adams catalyst, and 10 ml. of ethyl acetate was shaken at room temperature under an atmosphere of hydrogen until hydrogen absorption was complete. The hydrogen uptake was approximately five molar equivalents. After removal of catalyst and solvent, the residue was recrystallized from alcohol and yielded 45 mg. of yellow crystals, m.p. 125°.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 79.30; H, 7.45. Found: C, 79.40; H, 7.61.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

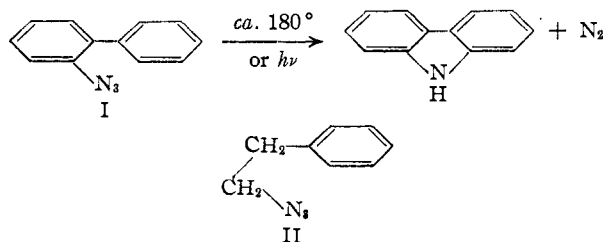
The Synthesis of Heterocyclic Compounds from Aryl Azides. I. Bromo and Nitro Carbazoles¹

BY PETER A. S. SMITH AND BERNARD BEAU BROWN²

A new reaction for the synthesis of carbazoles consists of the cyclization of *o*-azidobiphenyls by heat or ultraviolet light. Six bromo and nitro substituted carbazoles, three of them new, have been made by this reaction. A nitro group ortho to the azide group is shown to react in preference to the phenyl group, resulting in benzfuroxans.

Miscellaneous reports in the literature indicate that aromatic nuclei and unsaturated systems are susceptible to attack by hydrogen azide or organic azides under some conditions. The thermal interaction of hydrogen azide and *p*-xylene to give *p*-xylylidine,³ the photochemical formation of aniline from benzene and hydrogen azide,⁴ and the addition of phenyl azide to certain olefinic substances⁵ are examples. The adaptation of this type of reaction as a useful method of synthesis appeared to be a reasonable possibility, especially where intramolecular ring-formation could occur, and a search for instances of such reactions was made.

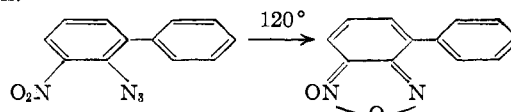
The work reported here is concerned with the behavior of *o*-azidobiphenyl and its derivatives, in which an opportunity is available for the formation of the stable, easily isolated carbazole nucleus. Cyclization was found to occur with *o*-azidobiphenyl (I) itself under the influence of heat or ultraviolet light, preferably in dilute solution, in yields as high as 76%. It may be of interest to



note that the cyclization of β -phenylethyl azide (II) to dihydroindole could not be obtained under any conditions, although the skeletal relationship of the azido group with respect to the benzene ring is the same as that of the azido group in *o*-azido biphenyl.

The high yields of carbazoles obtained in these reactions and the ease with which the reactions can

be carried out suggest that this may have value as a fairly general method for the synthesis of substituted carbazoles.⁶ For optimum results, a large ratio of solvent to azide is required; in solutions more concentrated than 1%, lower yields are usually obtained. The method has been applied to the synthesis of six other carbazoles, three of which are new, substituted with nitro and bromo groups, in yields not less than 74%. While nitro groups in most positions did not interfere, a nitro group in the *o'*-position led to dark, amorphous, uncrystallizable material; and a nitro group adjacent to the azido group led to furoxan formation.



In the case of 2-azido-3-nitrobiphenyl, the formation of phenylbenzfuroxan was indicated when the purified product of the reaction was found to melt 100° lower than the known 1-nitrocarbazole, although it gave the same analysis. In addition, the comparison of the ultraviolet and infrared absorption spectra of benzfuroxan, the suspected phenylbenzfuroxans and representative carbazoles supported this identification (Figs. 1 and 2). The sharp peaks in the ultraviolet spectra characteristic of the carbazole nucleus are absent from the spectra of the suspected benzfuroxans. No absorption band assignable to NH was found in the 2.9–3.2 μ region in the infrared spectra of the suspected benzfuroxans, but a band at 3.1 μ , assignable to associated NH, appeared in the spectrum of 3-nitrocarbazole in dioxane solution.

The formation of furoxans has previously been observed in the thermal decomposition of *o*-nitrophenylazides.⁷ Although furoxan formation is competitive with cyclization to carbazoles in the

(1) Presented at the National Meeting, American Chemical Society, San Francisco, California, March, 1949.

(2) From the doctoral thesis of Bernard Beau Brown, 1949.

(3) A. Bertho, *Ber.*, **59**, 589 (1926).

(4) R. N. Keller and P. A. S. Smith, *THIS JOURNAL*, **66**, 1122 (1944).

(5) K. Alder and G. Stein, *Ann.*, **485**, 211 (1931).

(6) For a summary of other syntheses of carbazoles, see E. C. Horning, M. G. Horning and G. N. Walker, *THIS JOURNAL*, **70**, 3935 (1948), and N. Campbell and B. M. Barclay, *Chem. Revs.*, **40**, 359 (1947).

(7) E. Noelting and K. Kohn, *Chem. Ztg.*, **18**, 1095 (1894).

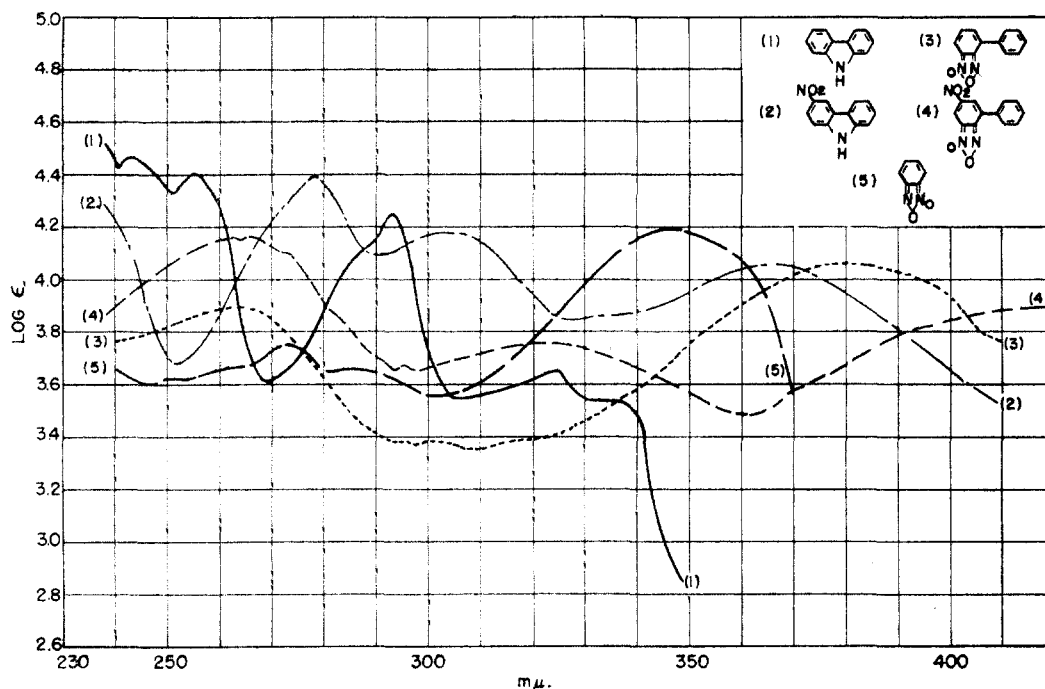


Fig. 1.

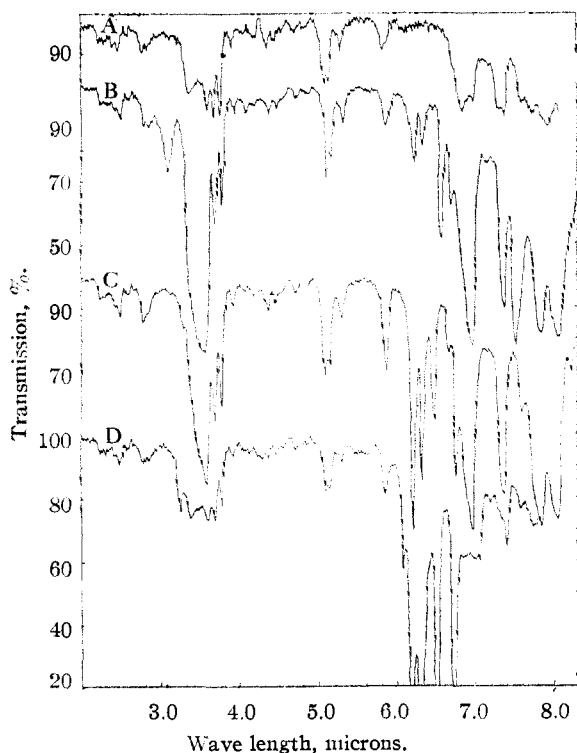


Fig. 2.—Infrared spectra: A, solvent only (dioxane); B, 3-nitrocarbazole; C, 4-phenylbenzofuroxan; D, benzofuroxan.

biphenyl series, the interaction between the azido and *o*-nitro groups seems to take place to the complete exclusion of carbazole formation. It also takes place at a much lower temperature (120°), although other conditions remain the same. Substituents in other positions of either ring did not noticeably affect the ease of carbazole formation

as indicated by the temperature required for decomposition and the qualitatively observed rate of nitrogen evolution. The identity of 2,7-dinitro carbazole, prepared for the first time, was confirmed by reduction to the known 2,7-diaminocarbazole.⁸

Reports of coupling reactions between phenyl azide and compounds containing "active" hydrogen have been in the literature for many years.⁹ We have not been able to detect such reactions with the *o*-azidobiphenyls; moreover, the cyclization of 2-azido-5-bromobiphenyl to 3-bromocarbazole can be carried out in the presence of large excesses of phenol, malonic ester or benzyl mercaptan in high yields. This may, however, only be evidence for the great ease of formation of the carbazole system. Strongly acidic media, however, have been shown to replace carbazole formation completely by another reaction.¹⁰

The photochemical cyclizations of the *o*-azidobiphenyls were in general not as satisfactory as the heat-induced reactions, both as to yields and reliability. The failure of radiation in the near ultraviolet to affect one of the azides (2-azido-5-nitrobiphenyl) suggests a dependence of threshold frequency upon structure, a subject on which we are not able to elaborate at this time.

The extension of the reaction to azidobiphenyls containing pyridine and thiophene rings has been reported,¹¹ and is the subject of communication II in this series.

(8) A. E. Porai-Koshits, *J. Gen. Chem. (U. S. S. R.)*, **14**, 1010 (1944).

(9) T. Curtius and G. Ehrhart, *Ber.*, **55**, 1559 (1922).

(10) P. A. S. Smith and B. B. Brown, *THIS JOURNAL*, **73**, 2438 (1951).

(11) P. A. S. Smith and J. H. Boyer, Abstracts of Papers Presented at the National Meeting, American Chemical Society, Chicago, Sept., 1950, p. 91N.

TABLE I
 CONVERSION OF *o*-AZIDOBIPHENYLS TO CARBAZOLES

Substituted <i>o</i> -azidobiphenyl	Product	M.p., °C.	Thermal Solvent	Yield, %	Solvent	Photochemical Yield, %
(<i>o</i> -Azidobiphenyl)	Carbazole	238-240 ^a	1,2,4-Trichloro- benzene	76 ^b	Tetralin	77
5-Bromo-	3-Bromocarbazole	195-196 ^c	Kerosene	83	Kerosene	23
5-Bromo-	3-Bromocarbazole	193-194	Phenol	65		
5-Bromo-	3-Bromocarbazole	194-196	Malonic ester	72		
5-Bromo-	3-Bromocarbazole	191-194	Benzyl mercaptan	66		
3,5-Dibromo-	1,3-Dibromocarbazole ^d	106-107	Kerosene	74	Tetralin	57
5-Nitro-	3-Nitrocarbazole	212-213 ^e	Kerosene	88	Kerosene	Recovered azide
4'-Nitro-	2-Nitrocarbazole	173-174 ^f	Kerosene	87	1,2,4-Trichloro- benzene	unidentified product ^g
5,4'-Dinitro-	3,7-Dinitrocarbazole ^h	325-326 ^k	Kerosene	94		^m
4,4'-Dinitro-	2,7-Dinitrocarbazole ⁿ	335-337 ^k	Kerosene	91	Tetralin	65
3-Nitro-	4-Phenylbenzofuroxan ^o	87.5-88.5	Kerosene	55	Kerosene	52
3,5-Dinitro-	4-Phenyl-6-nitrobenz- furoxan ^p	212-213	Kerosene	83	Tetralin	85
2'-Nitro-	No cryst. prod.					

^a Reported 238-240°, C. Graebe and C. Glaser, *Ann.*, **163**, 346 (1872). ^b Isolated as picrate, m.p. 184°. ^c Reported 198°, F. Muth and A. Schmelzer, German Patent 522,960; *Friedländer*, **17**, 725 (1932). ^d Calcd. for C₁₂H₇NBr₂: C, 44.31; H, 2.15. Found: C, 44.38; H, 2.26. ^e Reported 214°, F. Muth and A. Schmelzer, *ibid.*, **17**, 725 (1932). ^f Reported 175°, F. Muth and A. Schmelzer, *ibid.*, **17**, 725 (1932). ^g Dark amorphous solid, m.p. 300°. ^h Calcd. for C₁₂H₇O₄N₂: C, 56.03; H, 2.72. Found: C, 56.33; H, 2.86. ⁱ Air-bath. ^m Not suitable for photochemical treatment because of its insolubility. ⁿ Calcd. for C₁₂H₇O₄N₂: C, 56.03; H, 2.72. Found: C, 56.00; H, 2.79. ^o Calcd. for C₁₂H₉O₂N₂: C, 67.93; H, 3.77. Found: C, 68.16; H, 3.83. ^p Calcd. for C₁₂H₇O₄N₂: C, 56.03; H, 2.72. Found: C, 56.08; H, 2.77.

Experimental¹²

The preparation and description of the azides used in this work have been reported in another connection.¹⁰ Thermal decompositions of all the azides were carried out under essentially similar conditions, of which the following example is representative. The azides studied and the results obtained are recorded in Table I. Analyses¹³ are given only for new compounds.

2-Nitrocarbazole.—Four grams of 2-azido-4'-nitrobiphenyl was added in small portions to 400 cc. of kerosene (previously purified by shaking with concentrated sulfuric acid) maintained at 170-190°. The decomposition was nearly instantaneous, and evolution of nitrogen ceased almost at once after the final addition, but heating was maintained for 2-3 minutes longer. The solution was allowed to cool slowly to room temperature and was then chilled in the refrigerator for several hours. The crystals were removed by filtration, washed twice with 10-ml. portions of cold petroleum ether (b.p. 30-40°), and dried in an oven at 110° to constant weight. The yield of crude 2-nitrocarbazole was 3.07 g. (87%); m.p. 171-174°. Recrystallization from ethanol gave fluffy, brownish-yellow needles; m.p. 173-174°, with only small loss.

The photochemical decompositions of all azides were carried out under similar conditions, of which the following example is typical. The results are recorded in Table I.

1,3-Dibromocarbazole.—A solution of 1 g. of 2-azido-3,5-dibromobiphenyl in 20 ml. of tetralin contained in a quartz vessel was exposed to the radiation of a 100-watt mercury-vapor lamp. The evolution of nitrogen bubbles began in a few minutes; irradiation was stopped after three hours, when visible gas bubbles had ceased, although a fine spray could still be seen above the surface of the liquid. As no crystals appeared when the reaction mixture was chilled in the refrigerator for several hours or scratched while in an ice-salt-bath, the solution was concentrated to 5 ml. with a dry air stream on a hot-plate, and then blown down at room temperature to a light tan oil. Crystallization from aqueous ethanol gave 0.53 g. (57%) of 1,3-dibromocarbazole, m.p. 105-107°. Recrystallization gave a nearly quan-

titative recovery of very pale yellow crystals; m.p. 106-107°. A mixed melting point with the product, m.p. 106-107°, of the thermal decomposition of the same azide was undepressed.

Reduction of 2,7-Dinitrocarbazole.—2,7-Dinitrocarbazole (0.20 g.) was suspended in ethanol and hydrogenated in a Parr shaker with platinum oxide catalyst at room temperature and 40 lb. pressure. Evaporation of the filtered solution gave 0.14 g. of 2,7-diaminocarbazole, m.p. 259-261° (dec.). Porai-Koshits⁸ reports 258-260°.

β -Phenylethyl Azide.—To a solution of 37.5 g. (0.2 mole) of β -phenylethyl bromide in 60 ml. of 95% ethanol was added a suspension of 18 g. (0.43 mole) of sodium azide in 42 ml. of water. When solution was complete, a small further amount of solid sodium azide was added until a solid phase persisted. The resulting mixture was refluxed for 24 hr., cooled, poured into an equal volume of water and the precipitated oil was taken up with several portions of ether. The residue from the evaporation of the dried ether extracts boiled at 121-125° (20 mm.), wt. 21.5 g. (74%). A sample for analysis was redistilled at 0.5 mm.; b.p. 43°, n_{25}^D 1.5308, sweet, oppressive odor.

Anal. Calcd. for C₈H₉N₃: N, 28.55. Found: N, 28.78.

Ultraviolet Absorption Spectra.—The absorption curves given in Fig. 1 were determined with a Beckman quartz spectrophotometer, model DU, from 0.0005 molar solutions in 95% ethanol. The spectrum of benzofuroxan oxide, however, was kindly provided by Dr. Joseph H. Boyer of this department.

Infra-red Spectra.—The absorption curves given in Fig. 2 were determined with a Baird Associates double-beam infrared spectrophotometer with a sodium chloride prism, from 2% solutions in dioxane. The spectrum of 6-nitro-4-phenylbenzofuroxan, not given in Fig. 2, was also obtained; it was nearly identical with that of 4-phenylbenzofuroxan (Curve C) up to 6.9 μ , but lacked the bands at 6.95, 7.85 and 8.05 μ given by the latter compound. 3-Nitrocarbazole was also run in 1% solution in chloroform; the spectrum was the same except for the shift of the "associated NH" band at 3.1 μ to one at 2.9 μ for "unassociated NH."

(12) All melting points are uncorrected.

(13) Analyses by Microtech Laboratories, Skokie, Illinois.