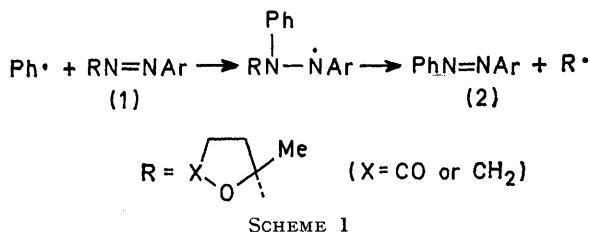# Intramolecular Addition of Aryl Radicals to the Azo-group; Synthesis and Properties of N-(Carbazol-9-yl)phenylaminyl Radicals
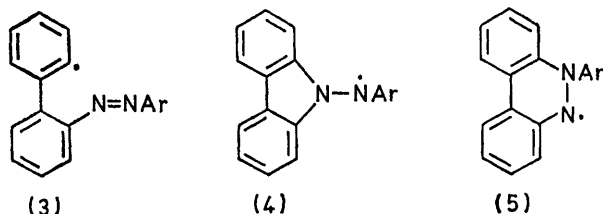
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2'-(Phenylazo)biphenyl-2-yl radicals (3; Ar = Ph), produced by reduction of 2'-(phenylazo)biphenyl-2-diazonium tetrafluoroborate (6) with potassium iodide at −20 °C, undergo intramolecular 1,5-addition to the azo-group, affording N-(carbazol-9-yl)phenylaminyl radicals (4; Ar = Ph), from which 1,2-dicarbazol-9-yl-1,2-diphenyl-hydrazine (8) is formed by N,N-coupling. The hydrazine (8) is thermally unstable and easily fragments at room temperature into aminyl radicals (4; Ar = Ph), which appear to undergo hydrogen abstraction and C,N-coupling as the major reaction paths.

ONLY a few examples of radical additions to azo-compounds have been reported. Additions of alkyl and benzoyl radicals have been shown proceed in both gas and liquid phase by radical-chain processes, leading to substituted hydrazines.[1] Aryl radical addition was not observed by Miller *et al.* in the reaction of phenyl radicals with azobenzene, only products of substitution in the aromatic rings were found.[2] More recently it has been reported that phenyl radicals react with arylazo-compounds (1) affording azobenzenes (2) by substitution at azo-nitrogen [3] (Scheme 1).

ation of 2,2'-diaminobiphenyl with nitrosobenzene (Scheme 2).

After addition of sodium iodide to a solution of compound (6) in acetone at −20 °C, 1,2-dicarbazol-9-yl-1,2-diphenylhydrazine (8) was isolated in 80% yield, indicating that 1,5-cyclization of the radical (3; Ar = Ph) had occurred, followed by N,N-dimerization of the resulting hydrazyl radical (4; Ar = Ph). No evidence of products from the alternative hydrazyl radical (5; Ar = Ph), was found.

The hydrazine (8) was identified on the basis of

SCHEME 1

In order to throw further light on the reactivity of aryl radicals towards azo-compounds we undertook a study of a number of 2'-arylazobiphenyl-2-yl radicals (3), in which intramolecular addition to the 2'-azo-group appears feasible and should lead to hydrazyl radicals (4) and/or (5) by 1,5- or 1,6-cyclization, respectively. We
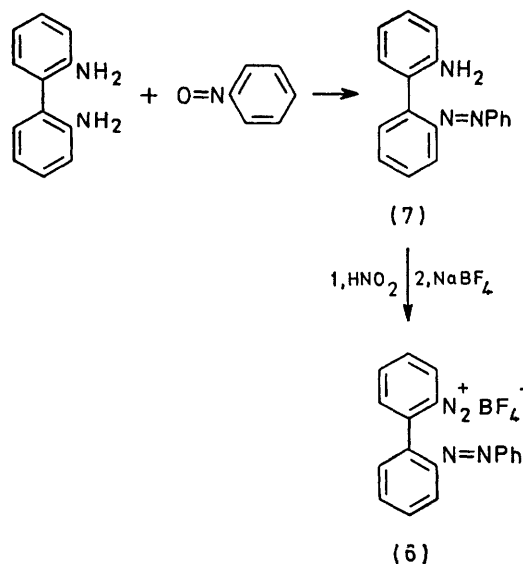

SCHEME 2

report here results obtained with 2'-phenylazobiphenyl-2-yl radicals (3; Ar = Ph), generated by reduction of the diazonium tetrafluoroborate (6) by iodide ions.[4] The tetrafluoroborate (6) was prepared from 2-amino-2'-phenylazobiphenyl (7), readily available by condens-

elemental analysis and spectroscopic and chemical evidence. The i.r. spectrum showed no NH stretching absorption, and the mass spectrum showed the molecular ion at m/e 514 (0.1%) and predominant fragment ions at 258 (61%), 167 (89), 166 (100), 140 (43), and 139 (33). The ion at m/e 258 arising from loss of $C_{18}H_{12}N_2$ from the molecular ion might be the N-carbazol-9-ylaniline

[1] O. P. Strausz, R. E. Berkeley, and H. E. Gunning, *Canad. J. Chem.*, 1969, **47**, 3470; H. S. Kharash, M. Zimmerman, W. Zimmt, and W. Nudenberg, *J. Org. Chem.*, 1953, **18**, 1045; O. F. Olaj, J. W. Breitenbach and I. Hofreiter, *Rec. Chem. Progr.*, 1969, **30**, 87.

[2] J. Miller, D. B. Paul, L. Y. Wong, and A. G. Kelso, *J. Chem. Soc. (B)*, 1970, 62.
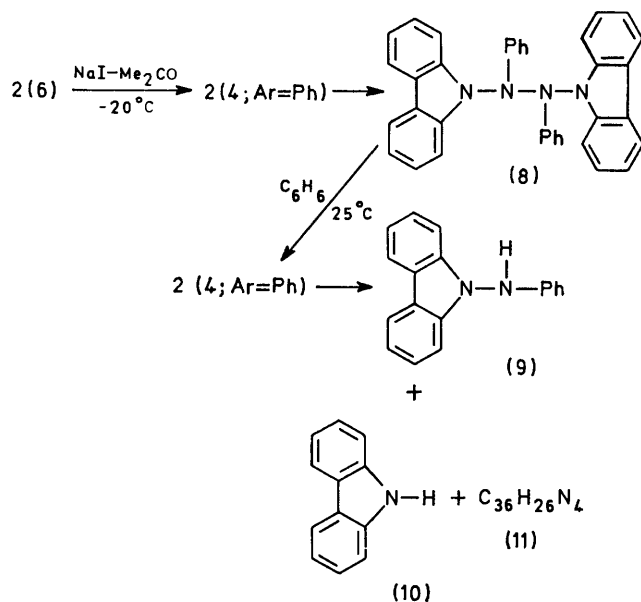[3] H. Lui and J. Warkentin, *Canad. J. Chem.*, 1973, **51**, 1148.
[4] D. H. Hey, G. H. Jones, and M. J. Perkins, *J.C.S. Perkin I*, 1972, 105.

ion, $C_{18}H_{14}N_2^+$; ions at m/e 167 and 166 deriving by fragmentation of $C_{18}H_{14}N_2^+$ can be assigned to the carbazole and carbazolyl species, $C_{12}H_9N^+$ and $C_{12}H_8N^+$, respectively, from which ions at m/e 140 and 139 are formed by loss of HCN. Unfortunately the structural assignment could not be confirmed by n.m.r. spectroscopy because of the low solubility of (8) in all solvents examined at the low temperature needed to prevent its decomposition. However the dimer (8) readily underwent thermal dissociation into hydrazyl radicals (4; Ar = Ph), and its structure is in agreement with the reported behaviour of aminyl radicals,[5] in which N,N-dimerization appears to be generally preferred over N,C- or C,C-dimerization.

The hydrazine (8) was stable as a solid in the dark, but decomposed slowly in light and particularly in solution, giving intensely coloured products. When a suspension of (8) in benzene was kept at room temperature for 24 h, complete decomposition occurred, and chromatography of the resulting mixture afforded N-carbazol-9-ylaniline (9) (20%), carbazole (10) (10%), and traces of a colourless product (11), as well as coloured products which were not identified (Scheme 3).

T.l.c. analysis of the crude mixture from decomposition of (8) showed substantial amounts of the
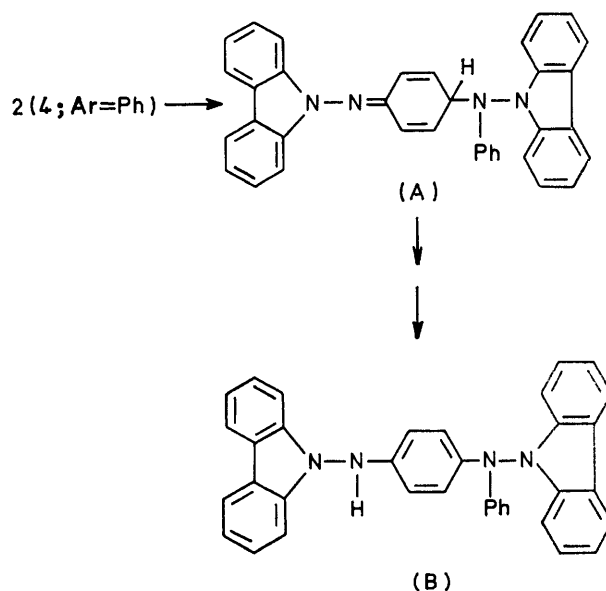

SCHEME 3

product (11), which could be isolated only in trace amounts since it was largely decomposed during column chromatography. Compound (11) was fairly stable as a solid, but decomposed in solution, particularly on treatment with lead dioxide and t-butyl hydroperoxide, giving carbazole (10) as the only identified product, together with intractable coloured products. The results of elemental analysis and the parent ion in the mass spectrum were consistent with the molecular

[5] W. C. Danen and F. A. Neugebauer, *Angew. Chem. Internat. Edn.*, 1975, **14**, 783.

formula $C_{36}H_{26}N_4$ for compound (11), thus pointing to another dimeric form of the hydrazyl radical (4; Ar = Ph). The i.r. spectrum showed a sharp NH stretching absorption at 3 340 cm^{-1} and the mass spectrum showed, besides the molecular ion at m/e 514 (1%), fragments at m/e 347 (82%) (arising from loss of carbazole), 167 (100), 166 (80), 140 (45), and 139 (38).

Compound (11) is tentatively assigned structure (B), derived by C_{para},N-coupling of the radical (4; Ar = Ph), leading to (A), followed by isomerization (Scheme 4).

SCHEME 4

This structural assignment is further supported by (i) the chemical behaviour of (11), *i.e.* its ready decomposition in solution leading to carbazole and blue products (probably arising from quinone di-imine derivatives) without affording any evidence of dissociation into hydrazyl radicals (4; Ar = Ph); (ii) our observations[6] that *para*-substituents in the aryl ring of hydrazyls (4), while not greatly affecting formation of dimers such as (8), prevent the formation of dimers analogous to (A), leading to products clearly derived from preliminary C_{ortho},N-coupling, and (iii) analogy with the structure of the elusive dimer postulated as the probable intermediate leading to the products of decomposition of triphenylhydrazyl radicals.[7]

From our findings it may be inferred that carbazolyl-hydrazyls (4; Ar = Ph) are very reactive radicals, which readily undergo N,N-dimerization at low temperature to give the hydrazine (8), which readily dissociates at room temperature to give back the radicals (4; Ar = Ph). At room temperature, hydrogen abstraction, leading to N-carbazol-9-ylaniline (9), and C,N-dimerization, most probably leading to (A) and

[6] L. Benati, P. Spagnolo, A. Tundo, and G. Zanardi, unpublished results.

[7] S. Goldschmidt, *Ber.*, 1920, **53**, 44; P. F. Holt and B. P. Hughes, *J. Chem. Soc.*, 1955, 1320.
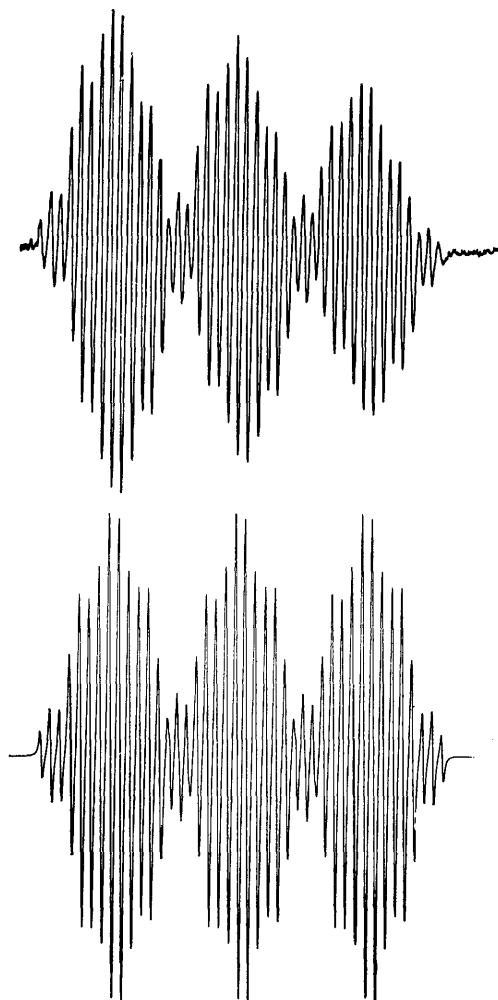
then to (B) by isomerization, appear to be the major reactions of the hydrazyls (4; Ar = Ph).

Further evidence for the thermal dissociation of the dimer (8) into reactive hydrazyl radicals (4; Ar = Ph) was obtained by e.s.r. spectroscopy. From a freshly degassed solution of (8) in methylcyclohexane at room temperature, the e.s.r. spectrum shown in the Figure was recorded. The hyperfine structure shows inter-

nitroxide (12). Structure (12) is further supported by the e.s.r. spectrum, which is identical with that derived from the dimer (8) obtained from photolysis of N-carbazol-9-ylaniline (9) in t-butyl hydroperoxide; formation of hydrazo-oxyl radicals from hydrazines in t-butyl hydroperoxide is well documented.[8]

Attempts to detect the hydrazyl radical (4; Ar = Ph) from dissociation of the dimer (8) by carefully degassing

Experimental (upper) and simulated e.s.r. spectra of the radical (12) at room temperature

action of the unpaired electron with two nitrogen atoms, $a_{N(1)}$ 11.8, $a_{N(2)}$ 1.8 G, and two different sets of protons, $a_{(3H)}$ 2.8, $a_{(2H)}$ 0.90 G, which can be most reasonably assigned to the ortho- and para-, and meta-protons of a phenyl ring. Since it is well known [8,9] that hydrazyl radicals show strong coupling of the unpaired electron with both nitrogen atoms [$a_{N(1)}/a_{N(2)}$ ca. 1.0—1.5] and g values of 2.0038 $\pm$ 0.0003, whereas for the radical investigated the $a_{N(1)}/a_{N(2)}$ value is ca. 6.5 and the calculated g factor 2.0054 $\pm$ 0.0002, characteristic of nitroxide radicals,[8] we identify the radical as the

the samples by high vacuum techniques were not successful, but the experiments performed provided evidence that the nitroxide radical (12) is less promptly formed under such conditions. Thus it appears that the hydrazyl radicals (4; Ar = Ph) are too short-lived to be observed by e.s.r. spectroscopy and that the only detectable radical species is the corresponding hydrazo-oxyl radical (12) produced by reaction of (4; Ar = Ph) with oxygen.

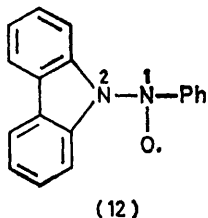The nitroxide radical (12) was not detected in solutions of compound (11) under the same conditions as employed

[8] V. Malatesta and K. U. Ingold, Tetrahedron Letters, 1973, 3311.

[9] L. Lunazzi and K. U. Ingold, J. Amer. Chem. Soc., 1974, 96, 5558.

for the dimer (8); all the experiments performed (including u.v. irradiation and treatment with lead dioxide or t-butyl hydroperoxide) showed decomposition of (11) (formation of intensely coloured solutions) without affording any detectable radical species.

Our results with 2'-phenylazobiphenyl-2-yl radicals (3; Ar = Ph) indicate that intramolecular 1,5-addition to the azo-group is favoured, leading to N-carbazol-9-yl-phenylaminyl radicals (4; Ar = Ph) and then to their

(12)

NN-dimerization products (8) in good yield. On this basis intramolecular cyclizations of 2'-arylazobiphenyl-2-yl radicals (3) appear to offer a convenient source of N-carbazol-9-ylarylaminyl radicals (4), suitable for a study of their as yet almost unknown chemistry.[10]

EXPERIMENTAL

I.r. data are for KBr discs. Mass spectra were recorded with a JEOL JHS-D100 spectrometer. E.s.r. spectra were obtained with a Varian V-4502 spectrometer, with V-4540 variable temperature accessory. Coupling constants were checked by computer simulation (Fortran IV program in which Lorentian lineshape was assumed); the g factor was determined by comparison with an aqueous solution of Fremy's salt. 2,2'-Diaminobiphenyl was prepared by reduction of commercial 2,2'-dinitrobiphenyl, and nitrosobenzene was a commercial product.

2-Amino-2'-phenylazobiphenyl (7).—Nitrosobenzene (3.2 g) in dichloromethane (20 ml) was added over 20 min to a solution of 2,2'-diaminobiphenyl (5 g) in 1 : 1 acetic acid–dichloromethane (100 ml). The resulting solution was refluxed on a steam-bath for 20 min, then poured into an excess of water and basified with sodium carbonate. The product was extracted with ether; evaporation of the extracts left an oily residue which was chromatographed on silica gel. Elution with 5% ether–petroleum afforded 2-amino-2'-phenylazobiphenyl (7) (2.5 g) as red needles, m.p. 58—59°, $v_{max.}$ 3 480 and 3 400 cm^{-1} (NH$_2$), m/e 273 (M^+, 73%), 257 (47), 181 (89), 168 (96), 167 (100), and 140 (15) (Found: C, 78.85; H, 5.6; N, 15.6. C$_{18}$H$_{15}$N$_3$ requires C, 79.1; H, 5.55; N, 15.4%).

Decomposition of the Diazonium Tetrafluoroborate (6).—2-Amino-2'-phenylazobiphenyl (7) (1.7 g) was suspended in hydrochloric acid (3 ml) and water (20 ml) and diazotized at 0 °C with sodium nitrite (0.48 g) in water (10 ml). After stirring at 0 °C for 1 h, a solution of sodium tetrafluoroborate (1 g) in water (10 ml) was added dropwise with stirring. The precipitated tetrafluoroborate (6) was washed with a little cold water and dried overnight. The salt (1.8 g) was then suspended in dry acetone (20 ml) and treated at −20 °C with a solution of sodium iodide (1.1 g) in acetone (10 ml). Nitrogen evolution was immediate followed by formation of a white precipitate, which after filtration and thorough washing with ether afforded 1,2-di-carbazol-9-yl-1,2-diphenylhydrazine (8) (1.05 g, 80%), m.p. 134—136° (decomp.), m/e 514 (M^+, 0.1%), 258 (61), 167 (89), 166 (100), 140 (43), and 139 (33%) (Found: C, 83.6; H, 5.2; N, 10.5. C$_{36}$H$_{26}$N$_4$ requires C, 84.0; H, 5.1; N, 10.85%).

Decomposition of the Dimer (8).—The dimer (8) (1 g) suspended in dry benzene (50 ml) was stirred at room temperature for 24 h, after which complete decomposition had occurred with formation of an intensely coloured solution. Removal of benzene left a residue which was rapidly chromatographed on silica gel under a nitrogen stream. Elution with 5% ether–petroleum afforded N-carbazol-9-ylaniline (9) (20%), as white plates, m.p. 170—172°, $v_{max.}$ 3 325 cm^{-1} (NH), m/e 258 (M^+, 100%), 257 (25), 166 (94), 140 (24), 139 (25), 92 (10), and 77 (6) (Found: C, 83.25; H, 5.55; N, 10.75. C$_{18}$H$_{14}$N$_2$ requires C, 83.7; H, 5.45; N, 10.85%). Elution with 10% ether–petroleum gave carbazole (10) (10%), identical with an authentic commercial sample. Elution with 15% ether–petroleum afforded compound (11) (ca. 1%), as white plates, m.p. 171—173° (decomp.), $v_{max.}$ 3 340 cm^{-1} (NH), m/e 514 (M^+, 1%), 347 (82), 167 (100), 166 (80), 140 (45), and 139 (38) (Found: C, 82.95; H, 5.2; N, 10.55. Calc. for C$_{36}$H$_{26}$N$_4$: C, 84.0; H, 5.1; N, 10.85%). Further elution with ether afforded a complex mixture of coloured products which could not be analysed.

Decomposition of Compound (11).—Compound (11) was stable in the dark, but fairly rapid decomposition was observed on exposure to light and especially in solution on treatment with lead dioxide and t-butyl hydroperoxide. In all cases examined t.l.c. showed decomposition to carbazole and a mixture of coloured products analogous to that isolated from decomposition of the hydrazine (8).

[7/112 *Received, 24th January, 1977*]

[10] A. R. Forrester, J. M. Hay, and R. H. Thomson, 'Organic Chemistry of Stable Free Radicals,' Academic Press, London, 1968, ch. 4.