Competitive Cyclisations of Singlet and Triplet Nitrenes. Part 5.[1] Mechanism of Cyclisation of 2-Nitrenobiphenyls and Related Systems

By **John M. Lindley, Ian M. McRobbie, Otto Meth-Cohn,*** and **Hans Suschitzky,** The Ramage Laboratories Department of Chemistry & Applied Chemistry, University of Salford, Salford M5 4WT, Lancashire

The conversion of 2-azidobiphenyl into carbazole is considered to involve concerted cyclisation of a singlet nitrene on the basis of the following evidence. (*a*) *N*-2-Nitrenophenyl heterocycles are poor sources of carbazole analogues since the concertedness of the cyclisation is impaired by the 'bridgehead' nitrogen. (*b*) 2-Methyl-2'-nitrenobiphenyl gives 4-methylcarbazole (up to 100% yield) under singlet-promoting conditions but increasingly more phenanthridine under conditions producing triplet nitrenes (heavy atom effect; photosensitised formation in acetophenone). By elevation of the photolysis temperature, azo-compound formation is diminished and phenanthridine yields are increased in photosensitised reactions. (*c*) 2,4,6-Trimethyl-2'-nitrenobiphenyl is shown to give both a carbazole and a phenanthridine at high temperatures (>300 °C) by way of a concerted attack of a singlet nitrene. The above principles are applied to the cyclisation of 2-(2-azidophenyl)-3,5-dimethylthiophen giving 2-methylthieno[3,2-*c*]quinoline. The role of solvents and additives during nitrene reactions is explored generally; tetrachlorothiophen and 2,3,5-tribromothiophen are solvents of choice for azide decompositions.

ONE of the most useful of nitrene reactions is the synthesis of carbazoles from 2-substituted biphenyls [*e.g.* (1) ⟶ (2) ⟶ (3)].[2] The yields are high and the reaction is little affected by substituents apart from 3-nitro- and -cyano-groups, which interfere with nitrene and hence carbazole formation. Even replacement of the phenyl ring (B) by a pyridyl or thienyl ring has little effect on the ease of cyclisation. However, although the intermediacy of a nitrene is well established, the mechanism of this reaction has been the subject of considerable controversy. Thus early work by Smolinsky suggested a triplet nitrene as the species most likely to be involved in carbazole formation.[3] This view was further supported by Reiser, from a study of the photolysis of 2-azidobiphenyl in a frozen matrix at 77 K whereby an intermediate was identified by its u.v. spectrum as probably the triplet nitrene,[4] and by the flash photolysis studies of Lehman and Berry, in which the same intermediate was recognized.[5] However, a study of the role of sensitizers and quenchers led Swenton and his co-workers [6] to prefer the involvement of a singlet nitrene,

[1] Part 4, I. M. McRobbie, O. Meth-Cohn, and H. Suschitzky, *J. Chem. Research*, 1977, (*S*) **17**; (*M*), 0434.

[2] *E.g.* P. A. S. Smith in 'Nitrenes,' ed. W. Lwowski, Interscience, New York, 1970, p. 129.

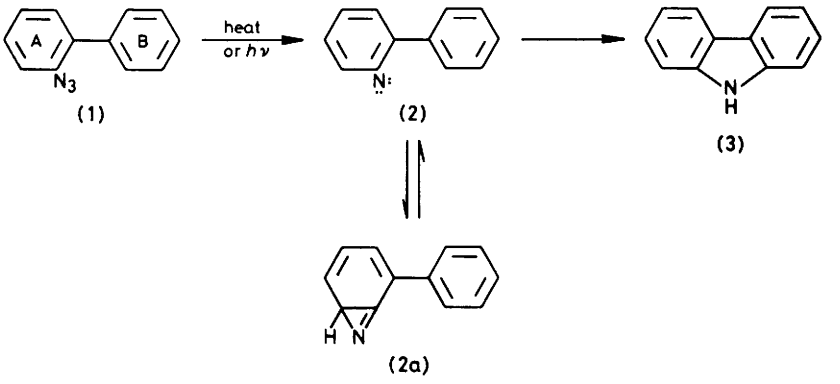
[3] G. Smolinsky, *J. Amer. Chem. Soc.*, 1961, **83**, 2489.

[4] A. Reiser, H. M. Wagner, and G. Bowes, *Tetrahedron Letters*, 1966, 2635; A. Reiser, G. Bowes, and R. J. Home, *Trans. Faraday Soc.*, 1966, **62**, 3162; A. Reiser, F. W. Willets, G. C. Terry, V. Williams, and R. Marley, *ibid.*, 1968, **64**, 3265.

[5] P. A. Lehmann and R. S. Berry, *J. Amer. Chem. Soc.*, 1973, **95**, 8614.

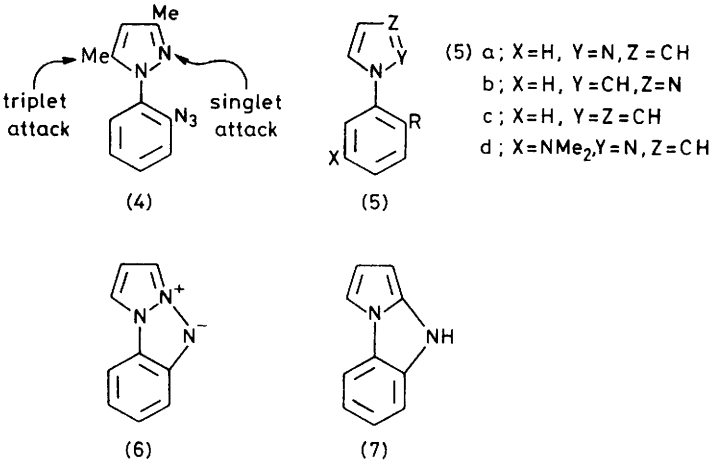
[6] J. S. Swenton, *Tetrahedron Letters*, 1968, 3421; J. S. Swenton, I. J. Ikeler, and B. H. Williams, *J. Amer. Chem. Soc.*, 1970, **92**, 3103.

since, for example, photolysis of 2-azidobiphenyl in a solution containing acetophenone (a triplet sensitizer) gave very little carbazole and mainly 2-azobiphenyl.* Sundberg [8] has produced clear evidence in favour of the singlet pathway for photolytically derived carbazole as follows. (*a*) The singlet arylnitrene is known to be in



equilibrium with an azanorcaradiene [(2) ⇌ (2a)] which may be trapped by amines to give an azepine.[8,9] Similarly, 2-nitrenobiphenyl can be diverted to give an azepine at the expense of carbazole formation in the presence of amines.[8a] (*b*) A more careful study of the flash photolysis [8b] of 2-azidobiphenyls excluded the triplet nitrene as the principal precursor of carbazole, since the decay of the intermediate observed by Reiser and by Lehman and Berry shows a different kinetic behaviour from that which results in carbazole.

During our investigation of the cyclisation of 1-(2-azidophenyl)-2,5-dimethylpyrazoles (4), we observed that singlet nitrene attack occurred at N-2 of the pyrazole ring, whereas triplet attack took place at the 5-methyl group.[10] However, precursors of the heterocyclic analogues of 2-nitrenobiphenyls bearing a 'bridgehead' nitrogen, such as the 2-nitro- and 2-azido-phenylpyrazole (5a; R = NO_2 or N_3) and 2-nitrophenylimidazole (5b; R = NO_2) and -pyrrole (5c; R = NO_2) were unusual in that cyclisation to a carbazole analogue at best proceeded only in poor yield (Table 1). Indeed, the pyrazole (5a; R = NO_2 or N_3) and the imidazole (5b; R = NO_2) gave no products from nitrene attack at the 5-CH, the former producing the pyrazolobenzotriazole (6) in low yield, and the latter only *o*-nitroaniline (despite the known stability of the expected cyclisation products). The pyrazoles appeared to undergo extensive ring opening giving unidentified, purple, nitrile-containing syrups. Even the 2-nitrenophenylpyrrole (5c; R = NO_2), containing a π-excessive ring prone to



* Lehman and Berry related this result to their own by suggesting that the azo-compounds arose from the triplet azide. This suggests that dimerisation of the azide proceeds faster than nitrogen loss, and implies that the reaction would be strongly concentration dependent, both of which are unlikely. Furthermore, the ubiquitous and efficient formation of azobenzene from nitrenes derived thermally, photochemically, or from sources other than the azide [*e.g. via* pyridylcarbene [7]) makes this argument unattractive.

[7] W. D. Crow and C. Wentrup, *Tetrahedron Letters*, 1968, 6149.

[8] (*a*) R. J. Sundberg, M. Brenner, S. R. Suter, and B. P. Das, *Tetrahedron Letters*, 1970, 2715; R. J. Sundberg and R. W. Heinzelman, *J. Org. Chem.*, 1974, **39**, 2546; (*b*) R. J. Sundberg, D. W. Gillespie, and B. A. DeGraff, *J. Amer. Chem. Soc.*, 1975, **97**, 6193.

[9] R. A. Abramovitch and E. P. Kyba in 'The Chemistry of the Azido Group,' ed. S. Patai, Interscience, New York, 1971, p. 257.

[10] I. M. McRobbie, O. Meth-Cohn, and H. Suschitzky, *Tetrahedron Letters*, 1976, 925.

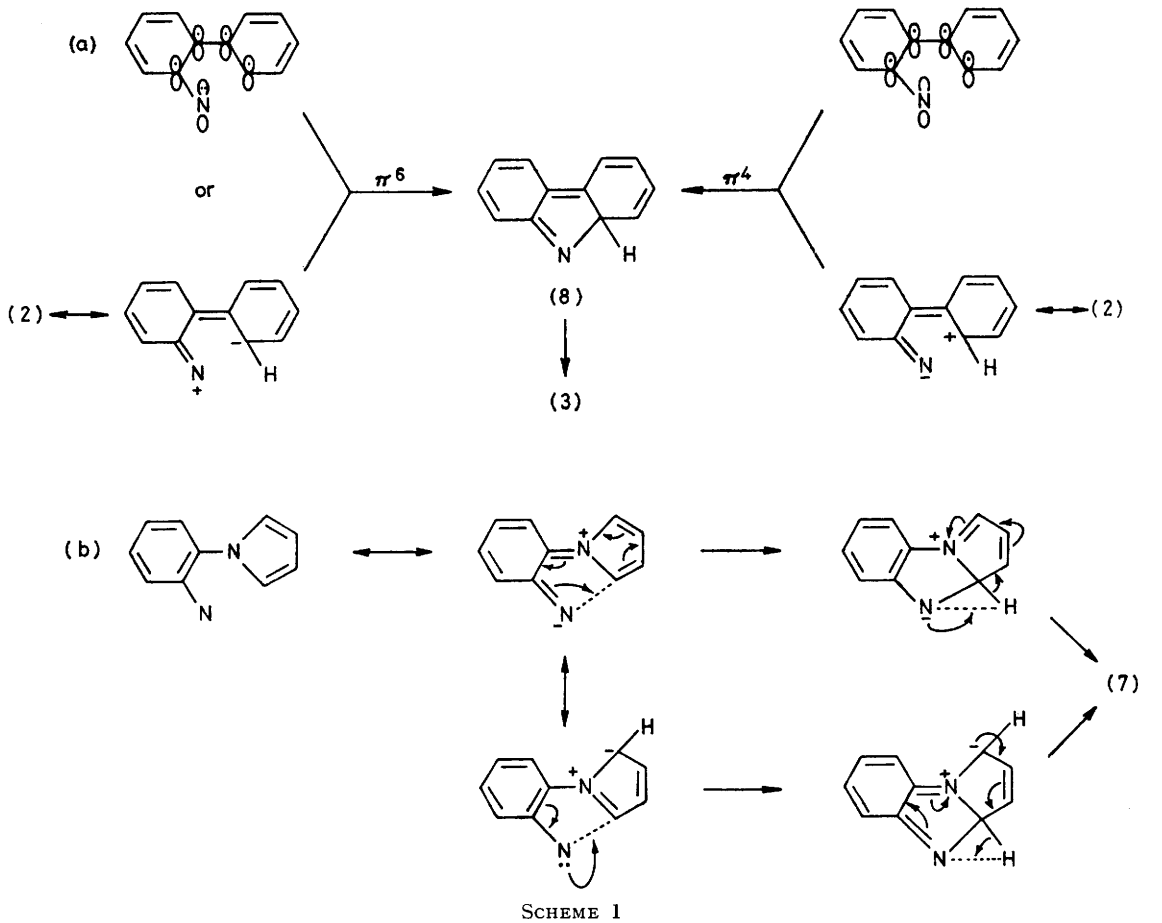
ready electrophilic substitution or addition, gave only a moderate yield of the carbazole analogue (7). Our earlier studies had shown that the presence of a *para*-dimethylamino-group rendered the singlet arylnitrene suspect. Moreover, the fact that the presence of a 'bridgehead' nitrogen in 2-azidobiphenyl heterocyclic analogues inhibits carbazole-type cyclisation suggested the need for a concerted cyclisation of the nitrene,

TABLE 1

Products from the decomposition of the azides and nitro-compounds (5a—d)

Substrate (5) R	Conditions: Heat or *hν*	Time (h)	Temp. (°C)	Solvent	Product(s) [%]
(5a) NO_2	Heat	10	152	Cumene, $(EtO)_3P$	(5a; R = NH_2) [19]
(5a) N_3	Heat	2	152	Cumene	(5a; R = NH_2) [19], (6) [15]
(5a) N_3	*hν*	72	Ambient	PhAc	(5a; R = NH_2) [16], azo-compound [35]
(5b) NO_2	Heat	10	152	Cumene, $(EtO)_3P$	*o*-Nitroaniline [29]
(5c) NO_2	Heat	10	152	Cumene, $(EtO)_3P$	(7) [26], *o*-nitroaniline (4)
(5d) NO_2	Heat	24	152	Cumene, $(EtO)_3P$	(5d; R = NO_2) [45], (5d; R = NH_2) [13]
(5d) N_3	Heat	2	156	PhBr	(5d; R = NH_2) [40]
(5d) N_3	*hν*	72	Ambient	PhAc	(5d; R = NH_2) [34]

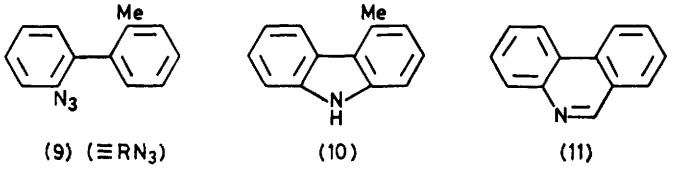
so stable as to be unreactive, and hence all the products were derived from the triplet nitrene.[10] Thus, when the (2-azido-5-dimethylaminophenyl)pyrazole (5d; R = N_3) gave only the corresponding amine under a variety of conditions (thermolysis in bromobenzene, photolysis in acetophenone, or triethyl-phosphite-catalysed deoxygenation of the 2-nitro-analogue) the triplet nitrene mechanism for carbazole formation in general became necessarily involving the singlet nitrene (Scheme 1). The non-reactivity of systems with 'bridgehead' nitrogen (5) would thus be explained, since the hetero-atom impairs this concertedness, only a higher energy electrocyclic pathway, involving charged, dipolar intermediates being possible [Scheme 1 (b)]. An interesting consequence of this mechanism arises from the dual role of the nitrene as a $_{\pi}2$ or $_{\pi}0$ component (depending upon



SCHEME 1

whether a full or empty orbital of the singlet nitrene is utilised) in the reaction, thereby enabling it to accommodate both electron-withdrawing and electron-releasing substituents (*cf.* AO and valence-bond representations in Scheme 1). This mechanism could then be regarded as a vinylogue of the well established singlet nitrene $\rightleftharpoons$ azanorcaradiene concerted interconversion, (2) $\rightleftharpoons$ (2a).

In order to establish firmly the role of the singlet nitrene in carbazole formation we have studied some model systems in which alternative intramolecular routes are available for the singlet and triplet nitrenes to follow. First, the cyclisation of 2-azido-2′-methylbiphenyl (9) [shown [11] to give the corresponding carbazole (10) in 91% yield by thermolysis in diphenyl ether] was reinvestigated. We argued that if only the singlet pathway led to carbazole, triplet conditions should favour phenanthridine (11) formation, by analogy with our earlier work with the pyrazoles (4).[10] The results are summarised in Table 2, from which the following significant points emerge. (*a*) Thermolysis invariably gave high yields of the carbazole (10). Thus, at 360 °C in liquid paraffin a 100% yield of the carbazole ensued, in line with our observations [1] that optimum yields are obtained at the highest possible reaction temperature.* However, in bromobenzene (which promotes singlet $\longrightarrow$ triplet interconversion by collisional deactivation of the nitrene [12]) phenanthridine (1.5%) was produced together with the carbazole (98%), while use of the better deactivator, 2,3,5-tribromothiophen, as solvent gave 4.5 and 95.5% of the same products, respectively. (*b*) Photolysis of the azide (9) was very revealing. Despite the low photolytic yields of carbazole (1) reported [11] (43% in cyclohexane), the use of methylene chloride (62%) (known to promote singlet pathways by lengthening the singlet lifetime [13]), or better still methylene chloride with added pyrene [6] (77%) (a triplet quencher and singlet sensitizer), made this route practicable. However, optimum yields were again realised by elevation of the temperature, so that photolysis at 107 °C in chlorobenzene gave the carbazole in 90% yield together with a little phenanthridine (4.5%), the amine RNH_2 (2%), and the azo-compound RN=NR (3.5%). Control experiments showed that negligible thermolysis of the azide occurred at this temperature. Direct irradiation of an aryl azide thus appears to give about a 9 : 1 ratio of singlet to triplet nitrene. (*c*) The results of photolysis of the azide in a triplet-sensitizing solvent were especially noteworthy. Swenton's results of irradiating 2-azidobiphenyl in solutions containing acetophenone have already been referred to.[6] We broadly concur with his findings; with acetophenone as solvent photolysis gave mainly 2-azobiphenyl (59%) and 2-aminobiphenyl (9.5%) with some carbazole (23.5%). The course of the reaction was little changed by conducting the photolysis at 107 °C (see Experimental section). However, when 2-azido-2′-methylbiphenyl (9) was similarly irradiated at ambient and at elevated temperature, a significant change in pathway was noted. Ambient conditions again favoured azo-compound formation (55%) with smaller amounts of amine (12.5%) and phenanthridine (9.5%), whereas elevation of the temperature considerably increased the yields of phenanthridine and the amine at the expense of the azo-compound.[14] Carbazole formation, however, remained consistent at 14—18%. Thus, at 96 °C, 28% of phenanthridine was formed together with 15% of azo-compound, whereas at 107 °C the yields were 36 and 5% respectively. Significantly, the amine (RNH_2) was formed in yields similar to those of the phenanthridine (generally slightly higher), suggesting that some amine was formed by dehydrogenation of the intermediate dihydrophenanthridine by the nitrene. In order to throw light on the origin of the amine and to optimise phenanthridine yields we conducted similar experiments with acetophenone in chlorobenzene, since arylnitrenes prefer to abstract aliphatic rather than aromatic hydrogen atoms.[4,15] Efficient photosensitisation still occurs in 10% solutions of acetophenone in chlorobenzene while at acetophenone concentrations of 5% carbazole yields are increased (to 37.5%). As expected, amine yields dropped significantly (12—19%), but curiously no increase in phenanthridine yield was observed. Indeed the total yield of isolated products dropped from 98.5 to 70% with this dilution, the remainder being the ubiquitous 'tar'. We interpret this as an indication of the need for spin-inversion of the first formed diradical (12) prior to ring closure to give the dihydrophenanthridine (Scheme 2). In competition with this pathway is the intermolecular coupling to give the polymeric amine (13) and, in suitable solvents, hydrogen abstraction to yield the amine RNH_2. Hydrogenolysis of the tar (extracted from the top of a chromatography column after elution of the products) over palladium–charcoal did indeed give some 2-amino-2′-methylbiphenyl. All the above photolyses were conducted with a 1% solution of the azide. Use of a 0.1% solution, which should favour the intramolecular pathway over polymerisation, caused a small increase in phenanthridine (39.5%) and amine (25%) formation and an increase in the overall yield of products (87%).



(9) (≡RN_3) (10) (11)

* 2-Amino-2′-methylbiphenyl and phenanthridine were unchanged at these temperatures.

[11] B. Coffin and R. F. Robbins, *J. Chem. Soc.*, 1965, 1252.

[12] See *e.g.* G. Anastassiou, *J. Amer. Chem. Soc.*, 1966, **88**, 2322; 1967, **89**, 3184.

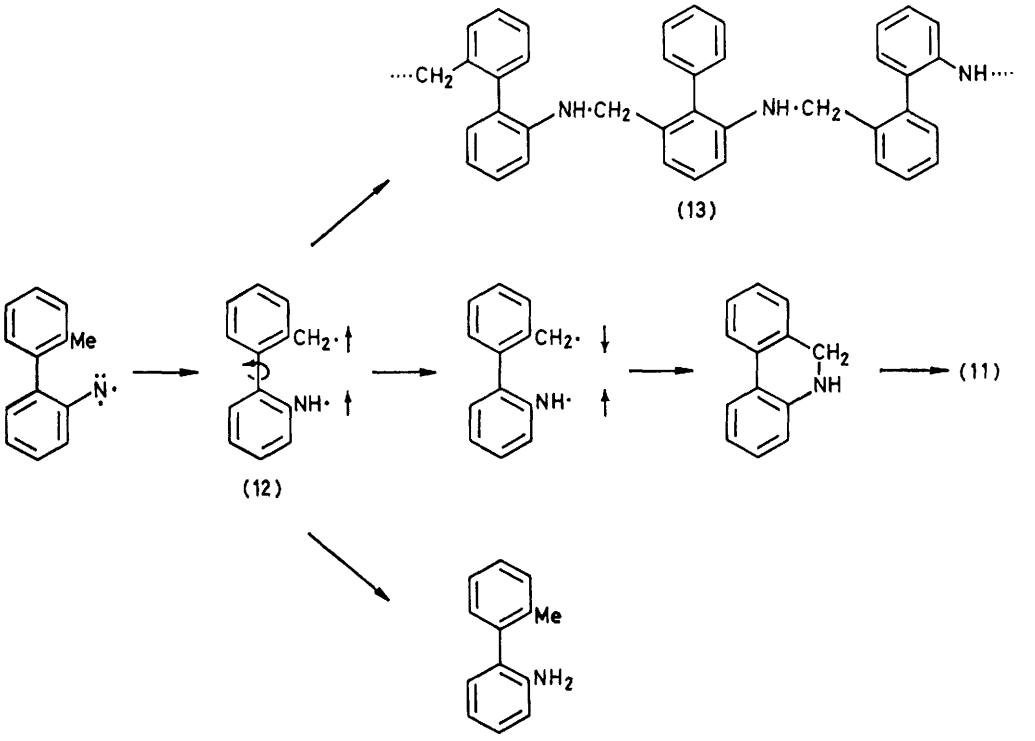
[13] R. Gleiter and R. Hoffmann, *Tetrahedron*, 1968, **24**, 5899; G. R. Felt, S. Linke, and W. Lwowski, *Tetrahedron Letters*, 1972, 2037.

[14] For a discussion of this temperature effect see J. M. Lindley, I. M. McRobbie, O. Meth-Cohn, and H. Suschitzky, *Tetrahedron Letters*, 1976, 4513.

[15] Ref. 9, p. 265 *et seq.*; ref. 2, p. 105 *et seq.*

The persistent formation of carbazole (15—18%) throughout all these acetophenone-photosensitised experiments (we have frequently noted similar yields of a wide variety of singlet products in competition with triplet alternatives during acetophenone-sensitised photolyses [1,10,14,16]) suggested the possibility of either competitive direct photolysis of the azide or the absorption of higher wavelength light by the azide than that utilised by the acetophenone. However, neither of these processes appears to be solely responsible for singlet product formation for the following reasons. (*a*) Photolysis of the azide in acetophenone solution at ambient temperature with acetophenone-filtered light produced mainly carbazole (64%) and no phenanthridine, but (*b*) photolysis of a solution of the azide in acetophenone at 96 °C through a solution of potassium dichromate (effectively leaving a window at about 312 nm since a Pyrex filter was used throughout) at two different strengths had no effect on carbazole yield (15 and 18%). (*c*) The above experiment in which a tenfold dilution of azide to solvent was employed (thus allowing a greater light absorption by the solvent relative to the azide) reduced the carbazole yield to 8%. (*d*) Use of a quartz apparatus instead of a Pyrex filter was accompanied by an increase in carbazole yield (25%). We therefore suggest that some mechanism exists for the contra-thermodynamic conversion of triplet into singlet nitrene, as hinted by Swenton.[6] Indeed we note a significant increase in the yield of carbazole (10) relative to the other products on photolysis of the azide (9) in hot 10% acetophenone in bromobenzene rather than chlorobenzene, suggesting that the heavy atom effect is capable of collisional activation as well as deactivation.

The significant temperature effect in acetophenone-sensitised photolyses is best explained as indicative of a reaction hierarchy.[1] The triplet arylnitrene produced at ambient temperature is evidently a very low energy species, since apparently unfavourable bimolecular reactions (formation of an azo-compound) compete successfully with attractive intramolecular alternatives. Only on thermal excitation does the energy of the species



SCHEME 2

effect C–H bond breaking and thus phenanthridine and amine formation. To underline further this sensitivity to temperature we irradiated the deuteriated biphenyl (14a) in acetophenone at 107 °C under the same conditions as its protio-analogue. Significantly, while carbazole formation was virtually unchanged (14%) a sixfold increase in azo-compound formation (30%) at the expense of mainly phenanthridine (threefold decrease) (13%) and of amine (27.5%) was observed. Clearly, the greater energy required to break the C–D than the C–H bond is responsible. Furthermore, mass spectral analysis of the deuterium content of the various products (Table 5) suggested that whereas the deuterium content of the azo-compound (14c) remains almost unaltered, significant loss of deuterium (*ca.* 10%) accompanies formation of the amine and phenanthridine (the latter might be expected to have a higher deuterium content if abstraction from CH is easier than from CD and no exchange occurred). The loss is even more marked in the

[16] I. M. McRobbie, O. Meth-Cohn, and H. Suschitzky, *Tetrahedron Letters*, 1976, 929.

TABLE 2

Products from the decomposition of 2-azido-2′-methylbiphenyl (9)

Thermal decomposition

Conditions			Products (%)					
Solvent [a]	Time (h)	Temp. (°C)	Unchanged azide (9)	Carbazole (10)	Phenanthridine (11)	Amine	Azo-compound	Total
Ph_2O [b]				91				91
Paraffin	1/6	360	0	100	0	0	0	100
PhBr	3	156	0	98	1.5	0	0	99.5
TBT [c]	3	156		95.5	4.5	0	0	100

Photolytic decomposition

Conditions				Products (%) *					
Solvent [a]	Temp. (°C)	Time (h)	Filter	Unchanged azide (9)	Carbazole (10)	Phenanthridine (11)	Amine	Azo-compound	Total
Cyclohexane [b]	Ambient	24		0	43				43
CH_2Cl_2–pyrene [d]	Ambient	24		0	77	0	0	0	77
$CHCl_2$		48		0	62	0	0	8	70
PhCl	107	8		0	90	4.5	2	3.5	100
PhAC	Ambient	48		0	17	9.5	12.5	55.5	94.5
PhAC	96	7		6.5	15	28	30	15	88.5
PhAc	107	8		1.5	18	36	39.5	5	97
PhAc	Ambient	8	PhCOMe	32	64	0	3.5	3	80.5
PhAc	96	16	K_2CrO_4 [e]	17	18	32.5	27.5	14	93.5
PhAc	96	20	K_2CrO_4 [f]	47	15	17.5	15	6.5	76
5% PhAc–PhCl	107	7		7	37.5	21	19	6.5	85
10% PhAc–PhCl	107	8		5	16	36	12	6	71
20% PhAc–PhCl	107	8		3	20.5	28	12	5	65.5
10% PhAc–PhCl	124	8		0	30	30	10.5	2	72.5
10% PhAc–PhCl [g]	99	10		8	8.5	39.5	25	12.5	87
10% PhAc–PhBr	107	8		11	27.5	33	36.5	2	98.5

* Yields based on azide consumed.

[a] A 1% solution was used unless indicated otherwise. [b] Lit.[11] result. [c] 2,3,5-Tribromothiophen. [d] Pyrene (3 g) added. [e] Aqueous 5×10^{-4}. [f] Aqueous 5×10^{-3}M-solution. [g] 0.1% Solution of azide.

TABLE 3

Products from the decomposition of 2-azido-2,4,6-trimethylbiphenyl (16)

Thermal decomposition

Conditions			Products (%)				
Solvent [a]	Time (h)	Temp. (°C)	Carbazole (18)	Phenanthridine (17)	Amine	Azo-compound	Total
n-$C_{16}H_{34}$ [b]		230	4.5	48	29	0	81.5
Cumene	4	152	0	23	71	0	91
PhBr	4	156	0	40	51	0	91
Ph_2O	3	192	0	41	27	0	68
Ph_2O	3/4	210	1.5	43.5	18.5	0	63.5
Ph_2O	1/6	237	4	45	32	0	81
Paraffin	4	150	0	19.5	79.5	0	99
Paraffin [c]	1/3	150	0	12.5	50	0	90.5 [d]
Paraffin [c]	1/6	200	4.5	28	56.5	0	89
Paraffin [c]	1/6	250	7	31.5	55.5	0	94
Paraffin [c]	1/6	300	8	32	47	0	87
Paraffin [c]	1/6	350	8	48	29	0	85
Paraffin [c]	1/6	390	8	58	27	0	93

Photolytic decomposition

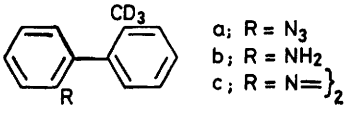
Conditions			Products (%) *					
Solvent [a]	Time (h)	Temp. (°C)	Unchanged azide	Carbazole (18)	Phenanthridine (17)	Amine	Azo-compound	Total
CH_2Cl_2	24	Ambient	0	0	0	16	15	31
CH_2Cl_2–pyrene [e]	24	Ambient	0	0	0	11	38	49
PhCl	8	107	19	0	22.5	33	21	81.5
PhAc	24	Ambient	0	0	0	7.5	68	75.5
PhAc	7.5	107	2	0	15	27.5	37	80
10% PhAc–PhCl	8	107	0	0	16	26	29	71

* Yields based on azide consumed.

[a] 1% Solution unless otherwise indicated. [b] Lit.[17] result. [c] 5% Solution used. [d] Yields based on azide consumed (25%). [e] Pyrene (3 g) added.

carbazole (19%), suggesting that autoxidative processes may be involved [*e.g.* (10) ⇄ (15) with the acetophenone being reduced to 1-phenylethanol] or rearrangement from an intermediate [related to (8)].* However, when *N*-deuteriated 4-methylcarbazole or 2-amino-2′-methylbiphenyl was irradiated in acetophenone no deuterium was incorporated at carbon. A fuller interpretation of these results requires further work and is outside the scope of this paper.

The above evidence strongly supports the view that carbazole is solely derived from the singlet nitrene whereas the triplet pathway leads to hydrogen abstraction (and hence amine, phenanthridine, and polymer) and dimerisation to the azo-compound.



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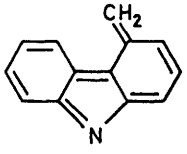

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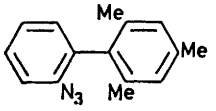

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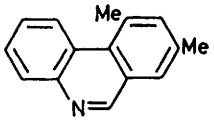

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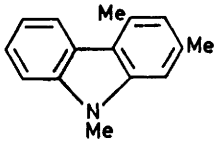
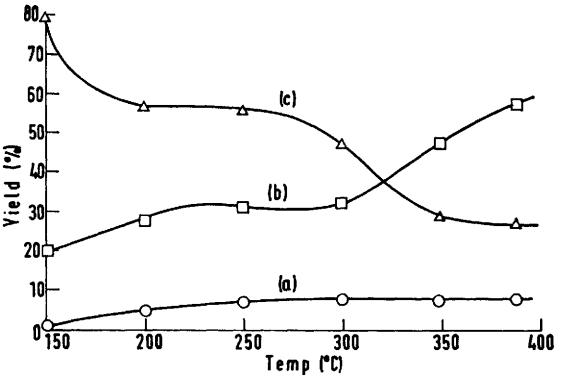


(18)

To further test the above ideas we have re-examined the decomposition of 2′-azido-2,4,6-trimethylbiphenyl (16). Smolinsky [17] noted that thermolysis of this azide in hexadecane (230 °C) gave mainly the phenanthridine (17) (48%), accompanied by a little of the carbazole (18) (4.5%) and the corresponding amine. This reversal is explicable on the basis of the concerted nitrene ⟶ carbazole mechanism (Scheme 1) since coplanarity of the two rings is a prerequisite for the orbital interactions depicted. Clearly, this is not easily obtained in a sterically constricted biphenyl. In this connection, whereas 3-nitro-2-phenylbenzo[*b*]thiophen readily cyclises with triethyl phosphite to a carbazole analogue, an indolobenzothiophen, the isomeric 2-nitro-3-phenyl isomer, does not. That this was due to the non-coplanarity of the phenyl and benzothienyl rings in the latter case (caused by *peri*-interactions) was underlined by comparison of u.v. spectra, which revealed steric interactions with the 3-phenyl-, but not with 2-phenylbenzothiophens.[18]

We expected that a suitable increase in temperature would eventually lead to conditions in which coplanarity was obtained and carbazole formation would be again significant. Table 3 and the Figure, which summarises the thermolysis of the azide (16) in various solvents at temperatures up to 390 °C suggest that a threshold temperature of at least 200 °C is necessary before any carbazole (18) is formed; and show that carbazole (18) yields increase with temperature up to about 250 °C but then increase no further, while a sharp increase in phenanthridine yields is observed above 300 °C. We account for this apparent anomaly by consideration of an alternative concerted process leading to phenanthridine, open to the singlet nitrene at higher temperatures in this series (Scheme 3).

This [1,6] sigmatropic shift again requires the appropriate coplanarity of the two rings and accounts for the preference for phenanthridine over carbazole formation at higher temperatures. A clear change in mechanism is indicated in the yield *vs.* temperature graph. Blank experiments demonstrated that the amine, carbazole (18), and phenanthridine (17), individually or mixed, were unchanged after heating in paraffin to 390 °C.



Yields of products from the decomposition of 2′-azido-2,4,6-trimethylbiphenyl in liquid paraffin at various temperatures: (a) 2,4,9-trimethylcarbazole (18), (b) 2,4-dimethylphenanthridine (17), (c) 2′-amino-2,4,6-trimethylbiphenyl

Photolysis of the same azide (16) in a variety of solvents at ambient or elevated temperature in no case yielded carbazole (Table 3). Furthermore, at ambient temperature in methylene chloride (with or without

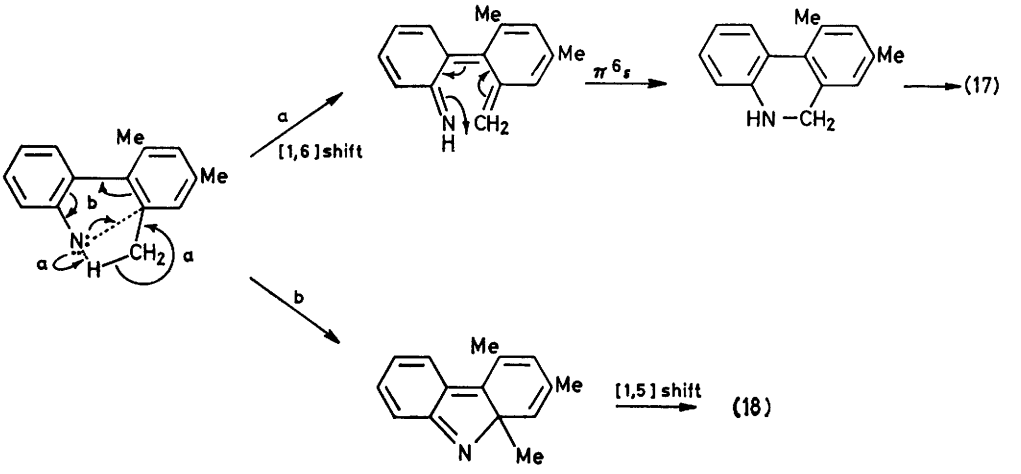
* A more reasonable explanation would involve charge-transfer interaction between the carbazole and acetophenone and subsequent hydrogen abstraction by the triplet ketone within the complex.

[17] G. Smolinsky, *J. Amer. Chem. Soc.*, **82**, 4717.
[18] K. E. Chippendale, B. Iddon, and H. Suschitzky, *J.C.S. Perkin I*, 1972, 2023.

added pyrene) or acetophenone, no phenanthridine was produced and considerable amounts of azo-compound were formed even at 107 °C. The results again support the contention that azo-compound formation is indicative of a 'lazy' triplet nitrene, whereas attack on a CH group required greater energy. The lower yields of the phenanthridine in this series as compared with those of the parent phenanthridine (11) under the same conditions are again due to the unfavourable proximity of the interacting centres in the former case (complete coplanarity should not be necessary for the triplet route to phenanthridines).

In conclusion, the above results speak strongly in support of the view that carbazole formation involves a singlet nitrene pathway involving a concerted mechanism which is a vinylogue of the well established singlet nitrene ⇄ azanorcaradiene interconversion. Triplet 2-nitrenobiphenyls and their analogues react by hydrogen abstraction or dimerisation rather than by carbazole formation.

We are now applying the above principles to a number of related systems, and to illustrate the synthetic value of the approach the results of the thermal and photolytic decomposition of 2-(2-azidophenyl)-3,5-dimethylthiophen (19) are appended (Table 4). We have shown earlier that singlet nitrene attack on thiophenic sulphur is either unfavourable or reversible,[14] and thus the only significant site for attack on (19) should be the 3-methyl group. At the usual temperatures employed for decomposition this will involve a triplet nitrene. Thus thermal decompositions gave increasing yields of the thienoquinoline (22) with increase in temperature and decrease in aliphatic hydrogen content of the solvent, optimum yields (65%) being obtained with tetrachlorothiophen. Tetrachlorothiophen and tribromothiophen are indeed a useful pair of solvents for thermally derived singlet and triplet nitrenes respectively since they (*a*) are easily made, (*b*) are inert, (*c*) are low melting and high boiling, and (*d*) offer no abstractable hydrogen. Photolysis again only achieved intramolecular C–H insertion at elevated temperatures as noted earlier. The use of singlet-promoting conditions (methylene chloride with and without pyrene) surprisingly gave solely the azo-compound (21), in line with our view that this is the last resort of a low energy triplet nitrene, derived in this case by intersystem crossing. Once more the results of sensitised photolyses in acetophenone changed from efficient azo-compound formation to inter- and intramolecular hydrogen abstraction with increasing temperature. Clearly, in cases where no convenient intramolecular route for the singlet nitrene is available, cyclisations are best accomplished thermally. When



SCHEME 3

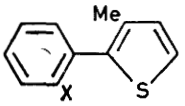
TABLE 4

Decomposition of 2-(2-azidophenyl)-3,5-dimethylthiophen (19)

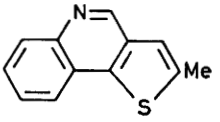
				Products (%)			
				Thienoquinoline	Amine	Azo-compound	
Method	Solvent	Time (h)	Temp. (°C)	(22)	(20)	(21)	Total
Heat	Decalin	1.5	190	34.5	39.5	0	74
Heat	Paraffin	1/6	230	53	16	0	69
Heat	TCT [a]	1/6	230	64.5	22.5	0	87
hν	CH_2Cl_2	48	Ambient	0	Trace	62	79 [b]
hν	CH_2Cl_2–pyrene [c]	72	Ambient	0	0	16.5	16.5
hν	PhAc	48	Ambient	0	45.5	45.5	91
hν	PhAc	8	107	30	66.5	0	96.5

[a] TCT = tetrachlorothiophen. [b] Azide (45%) recovered. [c] Pyrene (3 g) added.

such competition is possible sensitised photocyclisation is best for triplet-mediated processes.



(19) X = N_3
(20) X = NH_2
(21) X = N=$\}_2$



(22)

EXPERIMENTAL

General conditions are outlined in Part 3.[1] Photolysis at elevated temperatures were conducted by use of water (96 °C) or butan-1-ol (107 °C) in the Pyrex cooling jacket, heated under reflux by the heat of the u.v. lamp.

Synthesis of the Nitrene Precursors.—Syntheses of 2-azidobiphenyl,[19] 2′-azido-2,4,6-trimethylbiphenyl,[17] and 2-azido-2′-methylbiphenyl [11] were accomplished according to the literature methods.

(a) 1-(2-*Azidophenyl*)*pyrazole* (5a; R = N_3).—Pyrazole (6.8 g, 0.1 mol), *o*-fluoronitrobenzene (14.1 g, 0.1 mol), and anhydrous potassium fluoride (7 g) were heated together with stirring at 120—140 °C for 12 h. The cooled mixture was extracted with chloroform and the residue from the extract recrystallised from light petroleum to give 1-(2-nitrophenyl)pyrazole (5a; R = NO_2), m.p. 89° (18.3 g, 97%) (lit.,[20] 88—89°). The nitro-compound (5.0 g) was hydrogenated in ethanol (100 ml) over Raney nickel at ambient temperature and 100 atm. The filtered solution was evaporated and the residue distilled under vacuum after addition of zinc dust (*ca.* 1 g) to give 1-(2-*aminophenyl*)*pyrazole* (5a; R = NH_2) as a solid (3.1 g, 74%), m.p. 49°, b.p. 124° at 0.5 mmHg (Found: C, 68.0; H, 6.0; N, 26.0. $C_9H_9N_3$ requires C, 67.9; H, 5.7; N, 26.4%). The amine (7.95 g, 0.05 mol) in hydrochloric acid (35%, 15 ml) and water (15 ml) was cooled to 0 °C and diazotised with sodium nitrite (4.1 g, 0.06 mol) in water (10 ml), and the resulting solution was added with stirring to a solution of sodium azide (3.9 g, 0.06 mol) and sodium acetate (20 g) in water (100 ml). The resulting solution was extracted with ether (3 x) and the extracts were washed with aqueous 2M-sodium hydroxide and dried. The solution was percolated through alumina to give, after evaporation (below 40 °C), 1-(2-*azidophenyl*)*pyrazole* (5a; R = N_3) (7.3 g, 79%) as an oil, $\nu_{max.}$ (liquid film) 2 140 cm^{-1}, τ ($CDCl_3$) 1.83—2.80 (m) and 3.51 (t, *J* 2.5 Hz, pyrazole 4-H).

(b) 1-(2-*Azido*-5-*dimethylaminophenyl*)*pyrazole* (5d; R = N_3). 4-Chloro-1,2-dinitrobenzene [21] (5.0 g) and urea (2.0 g) in ethanol (50 ml) were treated with hydrazine hydrate (2.0 g), and the solution was set aside overnight. The crystalline mass was filtered off and recrystallised from ethanol giving (5-chloro-2-nitrophenyl)hydrazine (3.7 g, 76%), m.p. 165° (lit.,[22] 164°). To the hydrazine (3.75 g, 0.02 mol) in ethanol (100 ml) and hydrochloric acid (36%; 20 ml) was added malonaldehyde bis(dimethyl acetal) (3.3 g, 0.02 mol), and the mixture was refluxed for 3 h. On pouring onto ice a yellow solid was precipitated, which crystallised from ethanol to give 1-(5-*chloro*-2-*nitrophenyl*)-*pyrazole* (4.6 g, 97%) as cream plates, m.p. 58—59° (Found: C, 48.1; H, 2.5; N, 19.0. $C_9H_6ClN_3O_2$ requires C, 48.2; H, 2.7; N, 18.7%), τ ($CDCl_3$) 1.9—2.58(m) and 3.43(t, *J* 2.0 Hz, pyrazole 4-H). The nitro-compound (2.2 g, 0.01 mol), dimethylamine hydrochloride [1.1 g, 0.015M in water (5 ml)], and sodium hydrogen carbonate (2 g) in pyridine (50 ml) were boiled together overnight. The mixture was then poured onto water and the yellow precipitate filtered off and washed with water. Recrystallisation from ethyl acetate gave 1-(5-*dimethylamino*-2-*nitrophenyl*)-*pyrazole* (5d; R = NO_2) (2.0 g, 86%), m.p. 139—141° (Found: C, 56.8; H, 5.2; N, 24.0. $C_{11}H_{12}N_4O_2$ requires C, 56.9; H, 5.2; N, 24.1%), τ ($CDCl_3$) 2.10 (d, *J* 9 Hz, phenyl 3-H), 3.33—3.56 (m, phenyl 4- and 6-H), 2.31—2.50 (m, pyrazole 3- and 5-H), 3.63 (t, *J* 2.5 Hz, pyrazole 4-H), and 6.95 (s, NMe_2). The nitro-compound was reduced as above giving 1-(2-*amino*-5-*dimethylamino*)*pyrazole* (5d; R = NH_2) as an oil (82%), τ ($CDCl_3$) 2.40 (m, pyrazole 3- and 5-H), 3.73 (t, *J* 2.0 Hz, pyrazole 4-H), 3.43 (s, phenyl protons), 6.05br (NH_2), and 7.21 (NMe_2). The *azide* (5d; R = N_3) was also prepared as above (82%); $\nu_{max.}$ (film) 2 160 cm^{-1}, τ ($CDCl_3$) 2.14 (s, phenyl 3-H), 2.93—3.52 (m, phenyl 4- and 6-H and pyrazole 3- and 5-H), 3.71 (t, *J* 2.5 Hz, pyrazole 4-H), and 7.15 (s, NMe_2).

(c) 1-(2-*Nitrophenyl*)*imidazole* (5b; R = NO_2).—A mixture of imidazole (13.6 g), *o*-fluoronitrobenzene (28.0 g), anhydrous potassium fluoride (14.0 g) was heated and stirred at 120 °C for 24 h. On cooling the mass crystallised and was extracted with chloroform (500 ml); the extract was filtered and evaporated to give an orange solid. Recrystallisation from ethanol–benzene afforded 1-(2-nitrophenyl)imidazole (5b; R = NO_2) (33.8 g, 89%) as orange needles, m.p. 96—98° (lit.,[23] 94.7—97.2°).

(d) 1-(2-*Nitrophenyl*)*pyrrole* (5c; R = NO_2).—This was prepared according to the literature method,[24] m.p. 54—55° (lit.,[24] 54—55°).

(e) 2-*Azido*-2′-*trideuteriomethylbiphenyl* (14a). *o*-Nitrotoluene (45.7 g, 0.33 mol) was added to a solution of *O*-deuterioethanol (47.0 g, 1 mol) in which sodium (0.25 g) had been dissolved, and the mixture was heated under reflux for 20 h. The solvent was removed and the residue taken up in ether; the solution was washed with water, dried and evaporated. The oil was treated in the same manner with sodium deuterioethoxide three more times, after which the final product was distilled under vacuum giving *o*-nitrotrideuteriomethylbenzene (b.p. 75° at 2 mmHg) with 87.3% exchange of the methyl protons (mass spectrum). The nitro-compound was converted successively into the deuteriated toluidine and *o*-iodotoluene by Vogel's method [25] and thence into 2-nitro-2′-trideuteriomethylbiphenyl (14; R = NO_2) by the literature method.[11]

(f) 2-(2-*Azidophenyl*)-3,5-*dimethylthiophen* (19). A mixture of *o*-nitroaniline (28.0 g), aqueous hydrochloric acid (35%; 45 ml), and water (80 ml) was cooled to 0 °C and diazotised with sodium nitrite (14.5 g) in water (50 ml). The mixture was maintained at 0—5 °C for 1 h, filtered, and added to 2,4-dimethylthiophen (400 ml) at 0 °C.

[19] P. A. S. Smith and B. D. Brown, *J. Amer. Chem. Soc.*, 1951, **73**, 2435.
[20] I. L. Finar and R. J. Hurlock, *J. Chem. Soc.*, 1957, 3024.
[21] L. H. Welsh, *J. Amer. Chem. Soc.*, 1941, **63**, 3276.
[22] K. H. Menzel and H. Puetter, Belg. Pat. 643,807 (*Chem. Abs.*, 1965, **63**, 4440).
[23] A. L. Johnson, J. C. Kauer, D. C. Sharma, and R. I. Dorfman, *J. Medicin. Chem.*, 1969, **12**, 1024.
[24] G. W. H. Cheeseman and M. Rafiq, *J. Chem. Soc.* (*C*), 1971, 2732.
[25] A. I. Vogel, 'A Textbook of Practical Organic Chemistry,' 3rd edn., Longmans, London, 1967, p. 599.

Sodium acetate (80 g) in water (200 ml) was then added dropwise to the stirred and cooled (0—5 °C) mixture, and the solution was vigorously stirred for 3 h at 5—10 °C and then 48 h at ambient temperature. Extraction with chloroform (7 × 100 ml) gave, after combining and drying ($MgSO_4$) the extract, the excess of 2,4-dimethylthiophen (b.p. 137—138°) on distillation. The residue was absorbed onto alumina and eluted with light petroleum giving a yellow band (16.0 g, 34%) of *3,5-dimethyl-2-(2-nitrophenyl)-thiophen* as yellow crystals [from light petroleum (b.p. 80—100 °C)], m.p. 72—73° (Found: C, 62.0; H, 4.6; N, 6.2. $C_{12}H_{11}NO_2S$ requires C, 61.8; H, 4.75; N, 6.0%), M^+ 233, τ ($CDCl_3$) 1.91—2.61 (m, 4 phenyl protons), 3.36 (s, thiophen CH), 7.54 (s, Me), and 8.00 (s, Me). A mixture of the nitro-compound (15.0 g) in ethanol (50 ml), reduced iron (24.5 g), and ammonium chloride (17.4 g) in water (20 ml) was stirred and heated under reflux for 4 h. The hot solution was filtered and the residue and solution extracted with ether (3 × 100 ml). The combined extracts were dried and evaporated and the residue distilled under reduced pressure giving 2-(2-aminophenyl)-3,5-dimethylthiophen (20) (8.15 g, 62%) as a pale yellow oil, b.p. 154° at 2 mmHg, $\nu_{max.}$ (film) 3 470 and 3 380 cm^{-1} (NH_2), M^+ 203, τ ($CDCl_3$) 2.56—3.42 (m, 5 aromatic protons), 6.2br (NH_2), 7.55 (s, Me), and 7.95 (s, Me). The amine was converted into 2-(2-azidophenyl)-3,5-dimethylthiophen (19) (98%) in the above manner, giving a pale yellow oil, ν_{max} (film) 2 130 cm^{-1} (N_3), M^+ 229, τ ($CDCl_3$) 2.42—3.03 (m, 4 phenyl protons), 3.39 (s, thiophen CH), 7.57 (s, Me), and 7.95 (s, Me).

Decomposition of the Azides.—(a) *Thermolyses.* A solution (1%) of the azide (2.0 g) in the appropriate solvent (10 ml) was added to the heated solvent (190 ml) under nitrogen and the mixture was heated further (Tables 1—4) until the azide was absent or its amount minimal (i.r.). For experiments in which liquid paraffin was used a 5% solution was employed. Volatile solvents were removed under reduced pressure; paraffin, diphenyl ether, tetrachlorothiophen, and tribromothiophen were removed by elution of the mixture in light petroleum (b.p. 40—60 °C) through alumina with further light petroleum. Further elution with petroleum, or petroleum–diethyl ether gave successively the azo-compounds, amines, carbazoles, and phenanthridines or their thiophen analogues.

(b) *Photolyses.* The azide (1.0 g) in the appropriate solvent (100 ml) was purged with nitrogen and irradiated (Tables 1—3) under nitrogen until it was absent or its amount minimal (i.r.). Work-up was accomplished as for the thermolyses. Photolysis mixtures to which pyrene (3.0 g) had been added were first eluted slowly with light petroleum (b.p. 40—60 °C) to remove the pyrene.

(c) *Deoxygenations.* The nitro-compound (0.02 mol) was dissolved in cumene (190 ml; freshly filtered through a column of alumina) in a flask wrapped in aluminium foil and the stirred solution was purged with nitrogen and brought to reflux temperature. Freshly distilled triethyl phosphite (8.4 g, 0.05 mol) was then added rapidly. The reflux was maintained under nitrogen until the starting material was absent or its amount minimal (t.l.c. or high pressure liquid chromatography). The solvent, phosphites, and phosphates were removed under reduced pressure and the residual brown oil was chromatographed on alumina. The products from the various decompositions are recorded in Tables 1—4 and as follows: (i) 1-(2-aminophenyl)-pyrazole (5a; R = NH_2), eluted with ether; (ii) pyrazolo-[1,2-*a*]benzotriazole (6), eluted with light petroleum, m.p. 102° (lit.,[26] 102°); (iii) *2,2′-dipyrazol-1-ylazobenzene*, eluted with toluene–ether (1 : 1), m.p. 166—167° (lit.,[26] 167°); (iv) *o*-nitroaniline, eluted with light petroleum (b.p. 80—100°), m.p. 70° (lit.,[27] 71.5°); (v) *4H-pyrrolo[1,2-a]benzimidazole* (7), eluted with light petroleum (b.p. 80—100 °C) and recrystallised from the same solvent, m.p. 98—100° (Found: C, 76.75; H, 5.3; N, 18.0. $C_{10}H_8N_2$ requires C, 76.9; H, 5.2; N, 17.9%), $\nu_{max.}$ (Nujol) 3 400 cm^{-1} (NH), M^+ 156, τ ($CDCl_3$) 2.84—3.10 (m, 3 benzenoid H), 3.24—3.48, (3 H, m), 3.64—3.80 (1 H, m), and 6.47br (NH); (vi) *1-(2-amino-5-dimethylaminophenyl)pyrazole* (5d; R = NH_2), eluted with toluene–ether (10 : 1); (vii) 4-methylcarbazole (10), eluted with light petroleum–diethyl ether, m.p. 128—130° (lit.,[6] 129.5—130°); (viii) phenanthridine (11), eluted with light petroleum–diethyl ether, m.p. 104—105° (lit.,[28] 106°); (ix) 2-amino-2′-methylbiphenyl, eluted with light petroleum–diethyl ether; (x) *2,2′-bis-(2-tolyl)-azobenzene*, eluted with light petroleum and recrystallised from light petroleum (b.p. 80—100 °C), m.p. 149—151° (Found: C, 86.4; H, 6.1; N, 7.7. $C_{26}H_{22}N_2$ requires C, 86.15; H, 6.1; N, 7.7%), M^+ 362, τ ($CDCl_3$) 2.47—2.85 (aromatic) and 7.95 (s, Me); (xi) 2,4,9-trimethylcarbazole (18), eluted with light petroleum, m.p. 133—134° (lit.,[17] 134°); (xii) 8,10-dimethylphenanthridine (17), eluted with light petroleum–diethyl ether, m.p. 147—149° (lit.,[17] 149—150°); (xiii) 2′-amino-2,4,6-trimethylbiphenyl, eluted with light petroleum–diethyl ether, m.p. 97—98° (lit.,[17] 98—99°); (xiv) *2,2′-bis-(2,4,6-trimethylphenyl)azobenzene*, eluted with light petroleum and recrystallised from light petroleum (b.p. 80—100 °C), m.p. 198—199° (Found: C, 86.1; H, 7.1; N, 6.6. $C_{30}H_{30}N_2$ requires C, 86.1; H, 7.2; N, 6.7%), M^+ 418; (xv) *2-methylthieno[3,2-c]quinoline* (22), eluted with light petroleum–diethyl ether and recrystallised from light petroleum (b.p. 80—100 °C), m.p. 66—68° (lit.,[28]

TABLE 5

Deuterium content * of the precursor to, and products from decomposition of 2-azido-2′-trideuteriomethylbiphenyl (14a)

Compound	Exchange (%)	Deuterium content (%)												
		CH_3	CH_2D	CHD_2	CD_3	C_2H_6	C_2H_5D	$C_2H_4D_2$	$C_2H_3D_3$	$C_2H_2D_4$	C_2HD_5	CD_6	CH	CD
$2\text{-}NO_2\text{·}C_6H_4CD_3$	87.3	0	5.0	27.7	67.3									
(14a)	84.7	1.4	7.0	28.4	63.2									
(14b)	74.9	5.7	13.5	31.4	49.4									
(14c)	86.4					0	1.1	2.4	5.7	12.2	24.1	54.6		
4-[$^2H_3$]Methylcarbazole	65.7	9.1	22.7	30.6	37.6									
[10-^{1}H]Phenanthridine	74.9												26.0	74.0

* The method of Hill and Biemann (H. C. Hill, 'Introduction to Mass Spectrometry,' Heyden, London, 1966, p. 39; K. Biemann, 'Mass Spectrometry. Organic Chemical Applications,' McGraw-Hill, New York, 1962, ch. 5) was used to analyse the deuterium content from the mass spectral molecular ion intensities.

[27] L. Ehrenfeld and M. Puterbaugh, *Org. Synth.*, Coll. Vol. I, 1941, p. 388.

[28] E. C. Taylor and N. W. Kalenda, *J. Amer. Chem. Soc.*, 1954, **76**, 1699.

[26] B. M. Lynch and Y. Y. Hung, *J. Heterocyclic Chem.*, 1965, **2**, 218.

64.5—66°) (Found: C, 72.0; H, 4.4; N, 7.0. $C_{12}H_9NS$ requires C, 72.3; H, 4.55; N, 7.0%), M^+ 199, τ ($CDCl_3$) 1.16 (s, CH=N), 1.8—2.8 (m, 4 benzenoid H), 3.35 (s, thiophen CH), and 7.66 (s, Me); (xvi) 2-(2-aminophenyl)-3,5-dimethylthiophen (20), eluted with light petroleum–diethyl ether; (xvii) 2,2′-*bis*-(3,5-*dimethyl*-2-*thienyl*)*azobenzene* (21), eluted with light petroleum and recrystallised from light petroleum (b.p. 80—100°), m.p. 157—158° (Found: C, 71.6; H, 5.45; N, 7.1. $C_{24}H_{22}N_2S_2$ requires C, 71.6; H, 5.5; N, 7.0%), M^+ 402, τ ($CDCl_3$) 2.30—2.86 (m, 8 benzenoid H), 3.46 (s, 2 thiophenic H), 7.55 (s, 2 Me), and 7.99 (s, 2 Me).

Photolyses of 2-Azidobiphenyl.—When a 1% solution of 2-azidobiphenyl in acetophenone was irradiated in the above manner for 8 h the following products were obtained by chromatography through an alumina column.

(a) *At ambient temperature.* Elution with light petroleum gave 2-azidobiphenyl (36.5%) followed by 2-azobiphenyl (37.5%). Further elution with light petroleum–toluene (4 : 1) gave 2-aminobiphenyl (6%) followed by carbazole (16%). Based on azide consumed these yields are 59, 9.5, and 23.5%, respectively.

(b) *At* 107 °C. Using the same solvents, the products were the azide (7.5%), azo-compound (45.5%), the amine (6.5%), and carbazole (11.5%).

Photolysis of 2-Azido-2′-trideuteriomethylbiphenyl (14a).—The azide was irradiated in the usual manner at 107 °C in acetophenone solution (1%) for 8 h, giving on chromatography through alumina the following compounds in order of elution: azo-compound (30%) (light petroleum), amine (27.5%) [light petroleum–diethyl ether (19 : 1)], and a mixture of phenanthridine and carbazole [light petroleum–diethyl ether (19 : 1)] separated by extraction of an ethereal solution with aqueous hydrochloric acid (4M; 4 × 30 ml) and giving phenanthridine (13%) and the carbazole (14%).

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