The Pyrolysis of 2-Azidobenzoates. A New Synthesis of Carbazoles and Other N-Heterocycles [1]

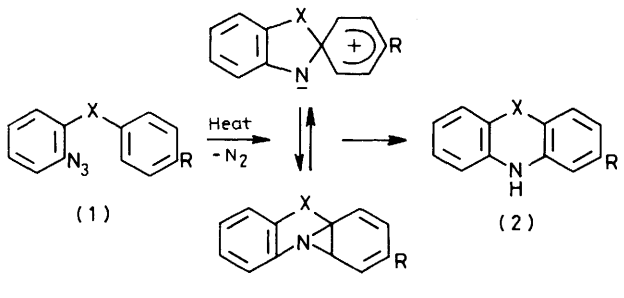
Michael G. Clancy, Massoud M. Hesabi, and Otto Meth-Cohn *,†
Ramage Laboratories, Chemistry Department, University of Salford, Salford M5 4WT

The spray pyrolysis of aryl 2-azidobenzoates yields carbazoles, involving a rearrangement whereby the nitrogen of the product is attached to the aryl 1-carbon, a process involving a spiro 6-membered intermediate. When the aryl *ortho*-positions were both alkyl substituted the product was an acridan instead. With an *ortho*-carboxylate, acridone formation competed with that of carbazole. When the CO–O group of the substrate was replaced by O–CO, CO–S, CO–NPh, or SO_2–O the pyrolysis was ineffective. Benzyl 2-azidobenzoates, however, pyrolysed to yield 1-benzyl-2,1-benzisoxazolones by an unprecedented C–O insertion reaction of the intermediate nitrene.

The thermolysis of *ortho*-substituted azidobenzenes of the type (1) to give various tricyclic products (2) involving an apparent rearrangement of the substituent R (Scheme 1) is well known and thoroughly studied.[2] Either a spiro-intermediate or an aziridine have been invoked as the intermediate in this process. Other novel pathways and products arise when the attacked benzene ring is 2,6-disubstituted. However, rather surprisingly, no examples have been reported in which the bridge (X) involves more than one atom. In this paper we have explored cases in which the link X involves two or three atoms.

It should be noted immediately that this omission is not too surprising since, in our experience, none of the chemistry discussed below is effective *in solution*,[3] while of those reactions mentioned above (Scheme 1) that we have attempted in the *vapour phase* the results were poor or fruitless.[4] We have shown elsewhere the particular virtue of 'spray pyrolysis' in the intramolecular chemistry of nitrenes.[5] This method was employed throughout this work. The substance is sprayed through a 0.5 mm capillary as a neat liquid or in its molten state into the pyrolysis tube. We first prepared a series of 2-azidobenzoyl esters (3) (Table 1) either by the interaction of 2-azidobenzoyl chloride and a phenol or alcohol in dry pyridine (Method A) or by heating isatoic anhydride with the hydroxy compound followed by the usual conversion of the 2-aminobenzoates into 2-azidobenzoates (3) (Method B).

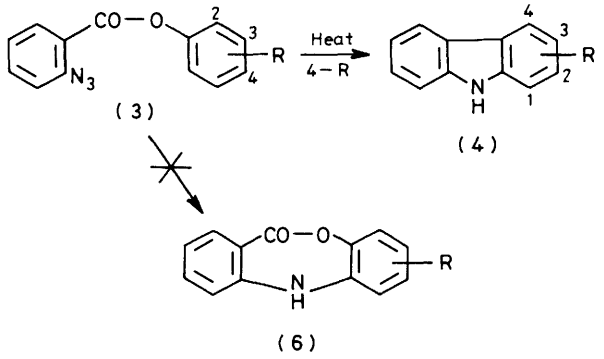
In two cases a benzyl halide and 2-azidobenzoic acid were allowed to interact in the presence of triethylamine to give the products (3w) and (3x) (Method C). The products were generally either oils or low melting solids, ideally suited to the spray pyrolysis conditions.



Scheme 1.

† *Present address:* National Chemical Research Laboratory, CSIR, P.O. Box 395, Pretoria 0001, Republic of South Africa.

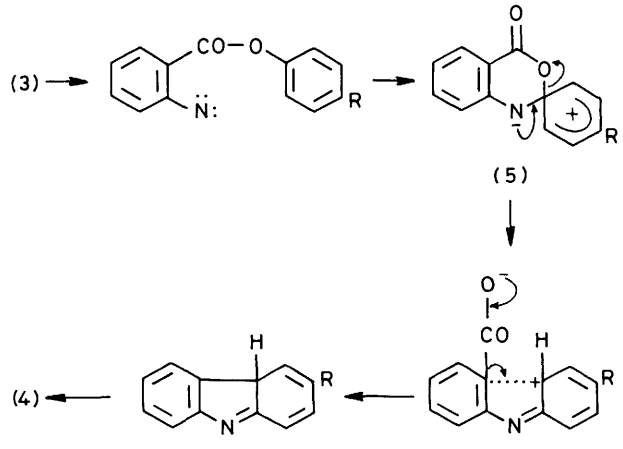
The pyrolysis of phenyl 2-azidobenzoate (3a) was first examined. The azide reacted at temperatures above 300 °C but the same product was formed from 300 to 750 °C. The reactions were generally rather tarry but gave optimum yields above *ca.* 380 °C. To our surprise the sole isolable product was carbazole. Curiously, the tarry by-products were at a minimum at the higher temperatures. A study of several substituted azidobenzoates quickly established that a rearrange-



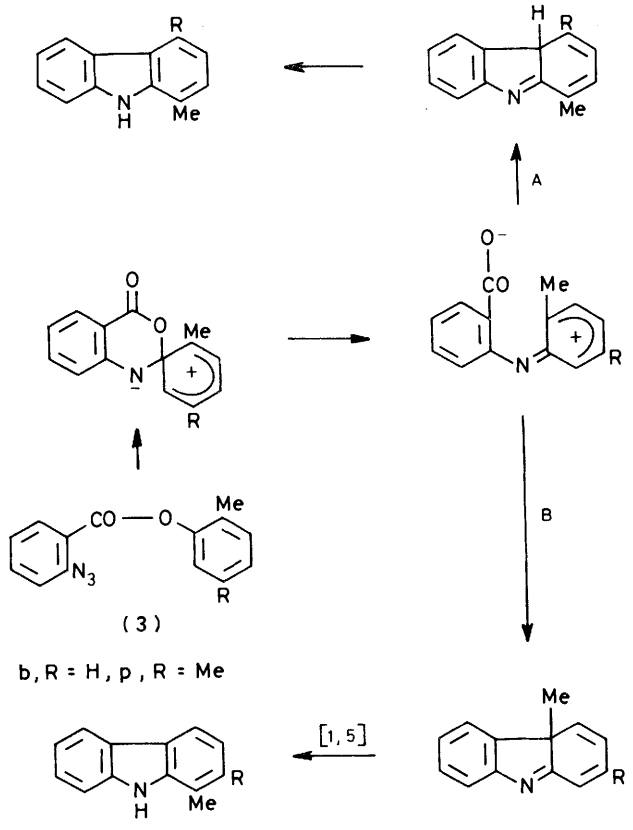
R	M.p. (°C)	Lit. m.p. (2-R) * (°C)	Lit. m.p. (3-R) * (°C)
Me	207	259 [b]	205 [c]
Cl	207	244 [d]	198—199 [d]
Br	199	250—251 [i]	199 [e]

* References *b*—*e* and *i* are given as footnotes to Table 2.

Scheme 2.

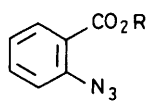


Scheme 3.



Scheme 4.

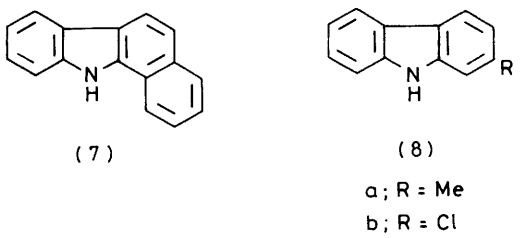
Table 1. The synthesis of 2-azidobenzoates (3)

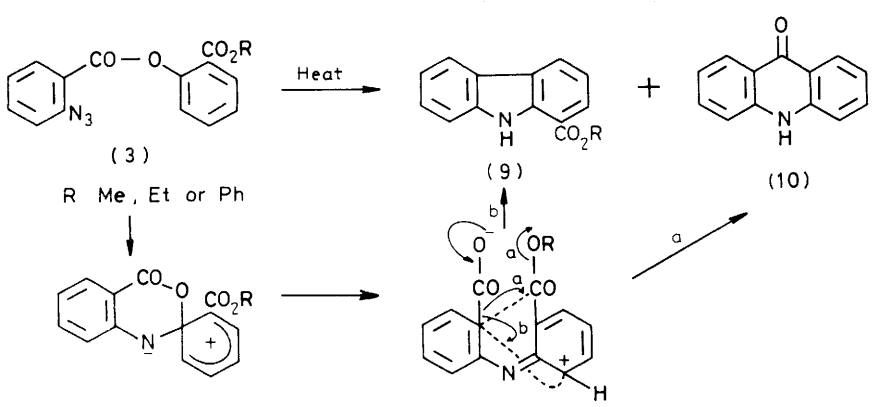


(3)

(3)	R	Method *	Yield (%)	M.p. (°C)
a	C_6H_5	A	96	50
a	C_6H_5	B	80	50
b	2-MeC_6H_4	A	65	Oil
c	3-MeC_6H_4	A	65	39
d	4-MeC_6H_4	A	61	Oil
e	4-$MeOC_6H_4$	A	80	70—72
f	C_6F_5	A	69	44—45
g	3-ClC_6H_4	A	69	56—58
h	4-ClC_6H_4	B	81	90
j	4-BrC_6H_4	B	78	76—78
k	2-$(CO_2Me)C_6H_4$	A	84	76—78
l	2-$(CO_2Et)C_6H_4$	A	70	57—58
m	2-$(CO_2Ph)C_6H_4$	A	53	69—70
n	2,4-$Me_2C_6H_3$	A	78	40—42
p	2,5-$Me_2C_6H_3$	A	87	49—50
q	2,6-$Me_2C_6H_3$	A	87	87—88
r	2,6-$(MeO)_2C_6H_3$	A	91	100—102
s	2,6-$Cl_2C_6H_3$	A	87	87
t	1-Naphthyl	A	74	73—75
u	2-Naphthyl	A	80	108—109
v	$CH_2C_6H_5$	A	73	Oil
w	$CH_2C_6H_4Me$-4	C	70	Oil
x	$CH_2C_6H_4Cl$-4	C	64	68—69
y	Et	A	88	Oil
z	Pr^i	A	92	Oil
aa	Bu^t	A	79	Oil
bb	CH_2CH_2Ph	A	79	Oil
cc	$CH_2CH{=}CHPh$	B	75	42—44

* For method see text.





R	(9) %	(10) %	Ratio 10 : 9
Me	14	22	1.5
Et	11	14	1.3
Ph	Trace	39	5.6

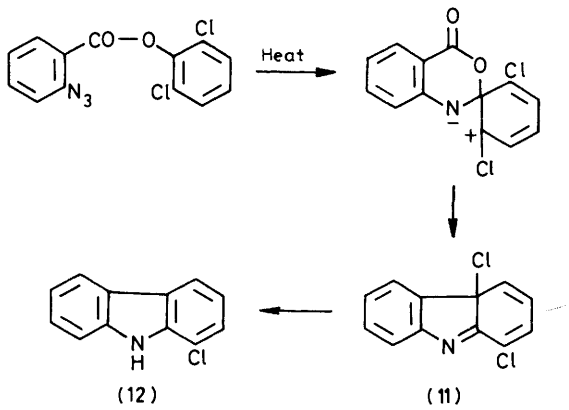
Scheme 5.

ment was involved as in Scheme 1. Thus 4-R-phenyl 2-azidobenzoates (3d), (3h), and (3j) in each case gave solely the 3-substituted carbazole (4), as shown by spectral, analytical, and melting point data (Scheme 2) as well as comparison with unambiguous samples (mixed m.p. and i.r. spectra). We explain the reaction by analogy with the mechanism shown in Scheme 1 (Scheme 3). The nitrene again prefers to attack by way of the spiro-intermediate (5), unique in that most nitrene reactions prefer a 5-membered intermediate. This intermediate, rather than rearranging to the (known [6]) dibenzoxazepinone (6) prefers to yield the thermodynamically more stable carbazole, presumably by a ring-opening ring-closure sequence. A variety of substituted phenyl 2-azidobenzoates reacted in an analogous manner (Table 2). However, in the case of 2-R-phenyl 2-azidobenzoates [*e.g.* (3b)] it is not certain that the 1-methylcarbazole that resulted arose from the pathway A (Scheme 4) or B, the latter involving a 1,5-methyl group shift. In order to clarify this mechanism we subjected the 2,5-dimethylphenyl azidobenzoate (3p) to pyrolysis. Path A would, in this case, give 1,4-dimethylcarbazole (m.p.,[7] 97—98 °C) whereas path B would yield the 1,2-isomer (m.p.,[8] 112—114 °C). In fact, solely the 1,4-isomer was obtained indicating that ring-closure occurs solely at the least substituted site where there is a choice (*i.e.* pathway A in Scheme 4). Similarly 2,4-dimethylphenyl 2-azidobenzoate (3n) gave solely 1,3-dimethylcarbazole. 1-Naphthyl azidobenzoate (3t) on pyrolysis gave solely the expected rearranged benzo[*a*]carbazole (7), albeit in low yield but the β-isomer proved too high melting to subject to spray pyrolysis.

Another surprising aspect of specificity was noted with the 3-R-phenyl azidobenzoates (3c) and (3g) which again each gave only one product, being the 2-isomer in each case.

No isolable product was obtained when the 4-methoxyphenyl or pentafluorophenyl azidobenzoates were pyrolysed. Nevertheless, we feel this route to carbazoles although only moderate in terms of yield has distinct synthetic virtue. The method is simple and preparatively useful (we have regularly pyrolysed 5-g samples and have used up to 20-g in certain cases). Above all, the starting materials are easily obtained from an anthranilic acid and a phenol, the substituents being capable of use in either ring and the reactions following predictable specificity.

In studying the *ortho*-substituents we next considered such systems with potentially reactive *ortho*-substituents. The family of salicyl azidobenzoates (3k,) (3l), and (3m) were examined and revealed a fascinating reactivity (Scheme 5). In all cases a mixture of a carbazole-1-carboxylic ester (9) and acridone (10) was produced but the ratio increased in favour

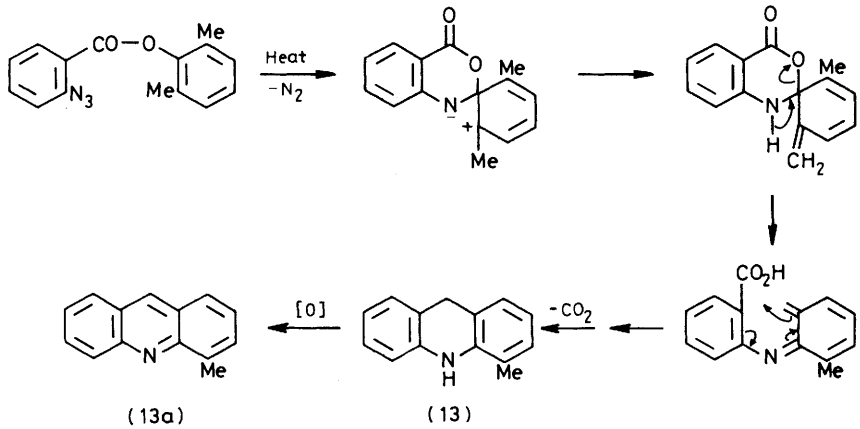


Scheme 6.

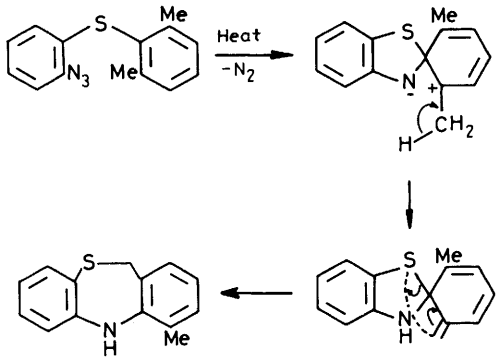
of the acridone in proportion to the leaving group efficiency of the OR group. It would thus appear that these two processes are in competition for the same intermediate.

We next turned our attention to 2,6-disubstituted benzoates and in particular examined the pyrolysis of the dimethyl (3q), dimethoxy (3r) and dichloro (3s) esters. As with the chemistry referred to above on compounds (1), new reaction pathways ensued. By analogy with 2-azidophenyl 2,6-dichlorophenyl sulphide [*cf.* (1; X = S)] which gave mostly 1-chlorophenothiazine together with a trace of the 4-chloro isomer,[2] we obtained only 1-chlorocarbazole (12) as product from 2,6-dichlorophenyl 2-azidobenzoate presumably as shown in Scheme 6. The 2,6-dimethylphenylbenzoate (3q) on pyrolysis did not yield a carbazole but instead gave an acridan (13) together with the corresponding acridine (13a) as an artefact. A reasonable rationale is shown in Scheme 7, which is related to the mechanism proposed for products formed from 2-azidophenyl 2,6-dimethylphenyl sulphide (Scheme 8).[2] As with the monomethoxybenzoates, the 2,6-dimethoxy derivatives gave only tar on pyrolysis.

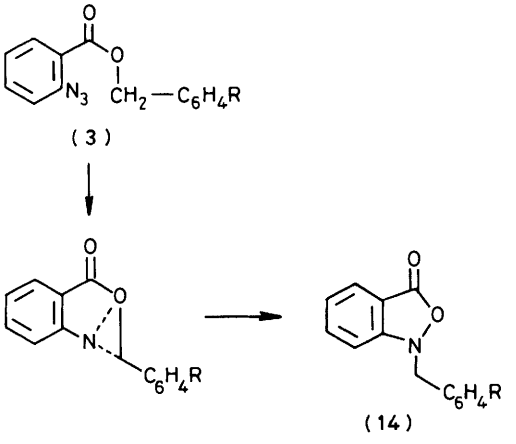
Having a general reaction type in hand we extended the study to a variety of other 2-azidobenzoyl esters. Aliphatic esters including ethyl, isopropyl, t-butyl, and phenethyl esters gave no clean products on pyrolysis. However the benzyl esters (3v), (3w), and (3x) proved most interesting, uncovering a new reaction type, to our knowledge unique in nitrene chemistry. On pyrolysis they did not yield products deriving from a 7-membered spiro-intermediate homologous with (5). Instead a C–O insertion was observed to give an *N*-benzylisoxazolone (14) (Scheme 9). The structure of the product (14; R = H) was readily confirmed by an unambiguous synthesis using Bamberger's method.[9] This involved the cyclisation of



Scheme 7.



Scheme 8.



R	Yield (%) of (14)
a; H	33
b; 4-Me	24
c; 4-Cl	16

Scheme 9.

2-hydroxylaminobenzoic acid to give benzisoxazolone followed by benzylation. It is not clear why this reaction was successful solely with the benzyl esters and not the other aliphatic esters. Presumably the phenyl ring stabilises the polar transition state by dispersal of the charge on the methylene.

Finally, we examined the pyrolysis of a number of analogues of the 2-azidobenzoates in which the CO–O bridge was varied. To our surprise no other system showed any evidence of a cyclisation reaction. Thus 2-azidophenyl 4-methylbenzoate (1; X = OCO, R = Me) gave no distinct product on pyrolysis while the *S*-(*p*-tolyl) 2-azidothiobenzoate (1; X = COS, R = Me) gave solely a trace of diphenyl disulphide as recognisable product. Similar failures were noted with a 2-azidobenzoyl amide (1; X = CONPh, R = H). However, from the 2-azidobenzenesulphonyl ester (1; X = SO_2O, R = H or Me) traces of carbazoles were isolated on pyrolysis at 750 °C.

In conclusion, the formation of carbazoles by pyrolysis of phenyl 2-azidobenzoates offers some distinct synthetic advantages over existing methods [10] in that, while the yields are moderate, the reaction utilises simple starting materials and allows diverse substitution patterns since substituted phenols are ubiquitous. The reaction is simple to perform and ideally suited to the preparation of gram quantities.

It deserves comment that a prominent peak in the mass spectra of the aryl 2-azidobenzoates (3) was due to an ion appropriate for the corresponding carbazole, probably as a result of thermal reaction prior to mass spectral breakdown.

Experimental

I.r. spectra were recorded on a Perkin-Elmer 257 spectrometer, ^{1}H n.m.r. spectra on a Varian EM360 (60 MHz) or Perkin-Elmer R32 (90 MHz) instrument, ^{13}C n.m.r. spectra on a Varian CFT20 (20 MHz) model, and mass spectra on AEI MS12 and AEI MS902s spectrometers. The pyrolyses were conducted as we described in the literature.[5a] Petroleum refers to the fraction of b.p. 60—80 °C and light petroleum to that of b.p. 40—60 °C. Column chromatography was conducted with Laporte type H alumina and type MFC silica (Hopkin and Williams).

Preparation of 2-Azidobenzoates (3).—*Method A.* To 2-azidobenzoyl chloride (3.5 g) in dry pyridine (15 ml, distilled from barium oxide) was added phenol (2.6 g) with stirring and ice–water cooling. After 20 min the mixture was poured into aqueous hydrochloric acid (250 ml; 2M) and the mixture extracted with ether (2 × 100 ml). The ethereal layer was washed with aqueous sodium hydroxide (2 × 50 ml; 5%) and then with water and dried over magnesium sulphate. Evaporation of the ether gave phenyl 2-azidobenzoate (3.8 g, 96%) as a white solid which crystallised as plates from light petroleum, m.p. 50 °C. In a similar manner were prepared the esters (3) recorded in Tables 1 and 3.

Method B. Aryl anthranilates were prepared by the method of Staiger and Miller [13] and converted into the corresponding azides by the method of Smith and Brown [14] to give the azides (3) recorded in Tables 1 and 3.

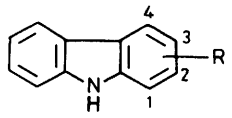
Method C. To a mixture of 2-azidobenzoic acid (5.0 g, 0.03 mol) and triethylamine (3.03 g, 0.03 mol) in dimethylformamide (50 ml) was added at 0 °C, with stirring, the appropriate benzyl chloride (0.03 mol) dropwise. The mixture was then heated to 60 °C for 6 h, after which it was poured into water (100 ml) and extracted with ether (3 × 50 ml). The ether layer was washed successively with hydrochloric acid (2M; 3 × 50 ml), sodium carbonate solution (10%; 2 × 50 ml), and water, and then dried and evaporated. The products were purified by elution through alumina with light petroleum–chloroform (9 : 1, v/v) to give the azides recorded in Tables 1 and 3.

Pyrolysis of 2-Azidobenzoates.—The azides were pyrolysed utilising the apparatus described previously.[5a] Samples of 2.5—5.0 g were pyrolysed at 1—2 mmHg at the temperature indicated in Table 2 and the products, also recorded in that Table, were isolated by extraction of the condensate with chloroform, absorption of this extract onto alumina, and chromatography. The carbazoles were eluted using light petroleum–ethyl acetate mixtures, or toluene. The acridan (13) and acridine (13a) were eluted with toluene, acridone (10) with toluene–chloroform (1 : 1), and the benzisoxazolones (14) with light petroleum–chloroform (1 : 2). Known products were identified by m.p., their i.r. and ^{1}H n.m.r. spectra and comparison with authentic material. Unknown products are indicated below.

(a) 1-*Benzyl*-2,1-*benzisoxazolone* (14a): white needles from petroleum (Found: C, 74.6; H, 5.0; N, 6.25. $C_{14}H_{11}NO_2$ requires C, 74.65; H, 4.92; N, 6.22%); $\nu_{max.}$ (Nujol): 1 760 cm^{-1} (C=O); δ ($CDCl_3$) 4.61 (s, CH_2) and 7.0—8.1 (m, aromatic H's); *m/z* 225 (M^+).

(b) 1-(4-*Methylbenzyl*)-2,1-*benzisoxazolone* (14b): $\nu_{max.}$

Table 2. The formation of carbazoles (4) and other products by pyrolysis of the azidobenzoates (3)



(4)

(3)	Pyrolysis temp. (°C)	Products No.	R	Yield (%)	M.p. (°C)	Lit. m.p. (°C)	Ref.
a	300	(4)	H	40	243—245	246	14
a	380	(4)	H	53			
a	500	(4)	H	33			
a	750	(4)	H	53			
b	300	(4)	1-Me	42	117—118	120	*a*
c	750	(4)	2-Me	22	259	259	*b*
d	300	(4)	3-Me	37	207	205	*c*
e	350	Tar					
f	400	Tar					
g	750	(4)	2-Cl	16	243	244	*d*
h	500	(4)	3-Cl	20	201	198—200	*d*
j	650	(4)	3-Br	15	199	199	*e*
k	420	(4)	1-CO_2Me	14	136—137	137	*f*
		(10)		22	354	354	*g*
l	420	(4)	1-CO_2Et	11—15	104	106—107	*f*
		(10)		14	354	354	*g*
m	400	(4)	1-CO_2Ph	7			
		(10)		39	354	354	*g*
		C_6H_5OH		28			
n	280	(4)	1,3-Me_2	13	188 *	188.5 *	*d*
p	350	(4)	1,4-Me_2	21	97	97—98	7
q	320	(13)		34	85—86	88	*h*
r	400	Tar					
s	330	(4)	1-Cl	16	123—125	125	*i*
t	400	(7)		9	224	228	*j*
v	300	(14a)		33	84—86		
w	340	(14b)		24	Oil		
x	300	(14c)		16	94—96		
y—cc	300—320	Tar					

* M.p. of picrate derivative.

[a] E. Campaigne and R. D. Lake, *J. Org. Chem.*, 1959, **24**, 483. [b] W. Borsche, *Liebigs Ann. Chem.*, 1904, **332**, 86. [c] S. Oakesholt and S. G. P. Plant, *J. Chem. Soc.*, 1926, 1212. [d] F. Ullmann, *Liebigs Ann. Chem.*, 1904, **332**, 96. [e] S. H. Tucker, *J. Chem. Soc.*, 1924, 1126. [f] M. Julia and M. J. Lenze, *Bull. Soc. Chim. Fr.*, 1962, 2263. [g] E. Bamberger, *Chem. Ber.*, 1909, **42**, 1707. [h] K. Lehmstedt, W. Burns, and H. Klee, *Chem. Ber.*, 1936, **69**, 2399. [i] B. Barclay and N. Campbell, *J. Chem. Soc.*, 1945, 530. [j] C. S. Barnes, K. H. Pausacker, and W. Badcek, *J. Chem. Soc.*, 1951, 730.

(liquid film) 1 760 cm^{-1} (C=O); δ ($CDCl_3$) 2.22 (s, Me), 4.65 (s, CH_2), and 6.9—7.8 (m, aromatic H's); *m/z* 239.0946 (M^+, $C_{15}H_{13}NO_2$ requires 239.0946).

(c) 1-(4-*Chlorobenzyl*)-2,1-*benzisoxazolone* (14c): white needles from ethanol (Found: C, 64.55; H, 4.0; N, 5.25. $C_{14}H_{10}ClNO_2$ requires C, 64.75; H, 3.88; N, 5.26%); $\nu_{max.}$ (Nujol) 1 760 cm^{-1} (C=O); δ ($CDCl_3$) 4.69s (CH_2) and 7.1—8.0 (m, aromatic H's); *m/z* 261/259 (M^+).

Unambiguous Synthesis of 1-*Benzyl*-2,1-*benzisoxazolone* (14a).—2-Nitrobenzoic acid (16.7 g), barium hydroxide (15.7 g), and ammonium chloride (7.5 g) in water (150 ml) at 10 °C were treated, with rapid stirring, with zinc dust (15.0 g) added portionwise while ensuring that the temperature did not exceed 20 °C. After a further 0.5 h the solution was filtered and the solid washed with warm water. The filtrate was acidified with 25% hydrochloric acid and the resulting yellow precipitate filtered off and dried in air, to give 2-hydroxylaminobenzoic acid (9.0 g, 51%), m.p. 141 °C (lit.,[9] m.p. 142 °C). This acid (5.0 g) was added in one portion to boiling M-sulphuric acid (50 ml) and the solution refluxed for 40 s, during which time it turned red; it was then rapidly cooled in ice, filtered, and the precipitate washed with water to give 2,1-benzisoxazolone (2.4 g, 63%) m.p. 110—112 °C, (lit.,[9] m.p. 112 °C). The compound decomposed on attempted recrystallisation from ethanol.

To a mixture of 2,1-benzisoxazolone (2.40 g) and benzyl bromide (3.10 g) in absolute ethanol was added a solution of sodium (0.46 g) in absolute ethanol (15 ml); the mixture was boiled under reflux for 0.5 h, and then cooled and poured onto ice (100 ml). The white precipitate was filtered off, washed with cold water, and dried to give 1-benzyl-2,1-benzisoxazolone (14a) (3.60 g, 90%) which on recrystallisation (petroleum) showed identical m.p. (84—86 °C), mixed m.p., i.r. and ^1H n.m.r. spectra to the sample prepared above.

Synthesis of Other Azides.—(a) 2-*Azidophenyl* p-*toluoate* (1; X = OCO, R = Me). Prepared as in Method A from 2-azidophenol [15] and *p*-toluoyl chloride (73%), as white needles from petroleum, m.p. 78—81 °C (Found: C, 66.55; H, 4.6; N, 16.65. $C_{14}H_{11}N_3O_2$ requires C, 66.40; H, 4.38; N, 16.59%).

(b) S-(p-*Tolyl*) 2-*azidothiobenzoate* (1; X = COS, R = Me).

Table 3. Properties of the 2-azidobenzoates (3)

(3)	Found C	Found H	Found N	Formula	Required C	Required H	Required N	Mass spectral fragments, *m/z* (*m/z* for halogen-containing ions is for lowest mass peak)
a								239, 211, 167, 146, 90
b				$C_{14}H_{11}N_3O_2$ [a]				253, 225, 181, 146, 90
c	66.65	4.3	16.35	$C_{14}H_{11}N_3O_2$	66.40	4.38	16.59	253, 225, 181, 146, 90
d				$C_{14}H_{11}N_3O_2$ [e]				253, 225, 181, 146, 90
e	62.25	4.15	15.85	$C_{14}H_{11}N_3O_3$	62.45	4.18	15.61	269, 197, 146, 90
f	47.45	1.25	12.8	$C_{13}H_4F_5N_3O_2$	47.43	1.22	12.71	329, 301, 257, 146
g	57.0	3.05	15.2	$C_{13}H_8ClN_3O_2$	57.05	2.95	15.35	273, 245, 201, 146, 90
h	57.2	3.15	15.3	$C_{13}H_8ClN_3O_2$	57.05	2.92	15.35	273, 245, 201, 146, 90
j	49.1	2.55	13.25	$C_{13}H_8BrN_3O_2$	49.08	2.53	13.21	317, 289, 245, 146, 90
k	60.35	3.8	14.1	$C_{15}H_{11}N_3O_4$	60.61	3.73	14.14	297, 269, 225, 195, 146, 9
l	61.5	4.2	13.65	$C_{16}H_{13}N_3O_4$	61.73	4.21	13.50	311, 283, 239, 146, 90
m				$C_{18}H_{17}N_3O_4$ [b]				167
n	66.9	3.75	11.5	$C_{20}H_{13}N_3O_4$	66.8	3.64	11.69	167
o	67.3	4.95	15.8	$C_{15}H_{13}N_3O_2$	67.41	4.90	15.71	267, 239, 195, 146, 90
p	67.35	4.9	15.8	$C_{15}H_{13}N_3O_2$	67.41	4.90	15.72	267, 239, 195, 146, 90
q	67.35	4.9	15.95	$C_{15}H_{13}N_3O_2$	67.41	4.90	15.72	267, 239, 195, 146
r	60.3	4.5	13.9	$C_{15}H_{13}N_3O_4$	60.10	4.38	14.04	299, 271, 146, 90
s	50.95	2.4	13.7	$C_{13}H_7Cl_2N_3O_2$	50.68	2.29	13.64	201
t	70.7	3.95	14.5	$C_{17}H_{11}N_3O_2$	70.58	3.83	14.53	289, 261, 217, 146, 90
u	70.6	3.9	14.55	$C_{17}H_{11}N_3O_2$	70.58	3.83	14.53	289, 261, 217, 146, 90
v				$C_{14}H_{11}N_3O_2$ [f]				
w				$C_{15}H_{13}N_3O_2$ [c]				
x	58.5	3.6	14.7	$C_{14}H_{10}ClN_3O_2$	58.44	3.50	14.61	289/287
y				$C_9H_9N_3O_2$ [g]				
z				$C_{10}H_{11}N_3O_2$ [d]				
aa				$C_{11}H_{13}N_3O_2$ [h]				
bb				$C_{15}H_{13}N_3O_2$ [i]				
cc	68.87	4.80	15.00	$C_{16}H_{13}N_3O_2$	68.81	4.69	15.05	279

[a] Found: M^+, *m/z* 253.0851; Calc. 253.0851. [b] Found: M^+, *m/z* 339.1221; Calc. 339.1219. [c] Found: M^+, *m/z* 267.1006; Calc. 267.1008. [d] Found: M^+, *m/z* 205.0852; Calc. 205.0851. [e] Found: M^+, *m/z* 253.0853; Calc. 253.0851. [f] Found: M^+, *m/z* 253.0849; Calc. 253.0851. [g] Found: M^+, *m/z* 191.0691; Calc. 191.0695. [h] Found: M^+, *m/z* 219.1007; Calc. 219.1008. [i] Found: M^+, *m/z* 267.1009; Calc. 267.1008.

Prepared as in Method A from 2-azidobenzoyl chloride and 4-methylthiophenol (69%) as cream needles from petroleum–ethyl acetate, m.p. 89 °C (Found: C, 62.6; H, 4.2; N, 15.4. $C_{14}H_{11}N_3OS$ requires C, 62.43; H, 4.12; N, 15.60%).

(c) *N-(2-Azidobenzoyl)diphenylamine* (1; X = CONPh, R = H). Prepared as in Method A from 2-azidobenzoyl chloride and diphenylamine in 85% yield as while crystals from ethanol, m.p. 109—110 °C (Found: C, 72.4; H, 4.45; N, 18.0. $C_{19}H_{14}N_4O$ requires C, 72.59; H, 4.48; N, 17.82%); $\nu_{max.}$ (Nujol) 2 200 (N_3) and 1 660 cm^{-1} (C=O).

(d) *Phenyl and* p-*tolyl 2-azidobenzenesulphonates* (1; X = SO_2O, R = H *and* Me *respectively*). 2-Nitrobenzenesulphonyl chloride was allowed to react as in Method A with phenol and *p*-cresol, respectively, and the crude products reduced as follows. To a boiling mixture of reduced iron (3.6 g), ammonium chloride (0.4 g), and water (20 ml) was added with rapid and efficient stirring the above nitro compound (0.02 mol) in ethanol (80 ml) and the stirring and reflux maintained for 3 h. The hot solution was filtered and cooled to precipitate the 2-aminobenzenesulphonyl esters in 61 (m.p. 70 °C) and 68% yield (m.p. 75—76 °C) respectively; $\nu_{max.}$ (Nujol) 3 460 and 3 380 cm^{-1} (NH_2). These amines were converted into the corresponding azides by Method B to give *phenyl 2-azidobenzenesulphonate*, white crystals from ethanol, m.p. 118—121 °C (66%) (Found: C, 52.15; H, 3.35; N, 15.35. $C_{12}H_9N_3O_3S$ requires C, 52.35; H, 3.29; N, 15.26%); $\nu_{max.}$ (Nujol) 2 150 cm^{-1} (N_3); and p-*tolyl 2-azidobenzenesulphonate*, as white crystals from ethanol, m.p. 103—105 °C (71%) (Found: C, 54.0; H, 3.7; N, 14.65. $C_{13}H_{11}N_3O_3S$ requires C, 53.96; H, 3.83; N, 14.52%).

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