The Photolysis of *o*-Azidobenzoic Acid Derivatives: a Practicable Synthesis of 2-Alkoxy-3-alkoxycarbonyl-3*H*-azepines

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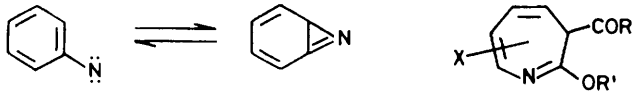
Photolysis of several *o*-azidobenzoic acid derivatives (*o*-$N_3C_6H_4COR$; R = OH, Cl, OMe, OPh, SPh, NH_2, NHAr, and OBz) in methanol, or methanol–tetrahydrofuran solution, yields in the majority of cases 3-substituted 2-methoxy-3*H*-azepines. Substituted methyl 2-azidobenzoates (X-2-$N_3C_6H_3CO_2Me$; X = Cl, OMe, NO_2, Br, CO_2Me, and CO_2H) give the correspondingly substituted 2-methoxy-3-methoxycarbonyl-3*H*-azepines depending on the nature and position of the substituent group (X). In contrast, thermolysis of methyl *o*-azidobenzoate in alcohol solution gives mixtures of 3*H*-azepines and triplet nitrene derived products.

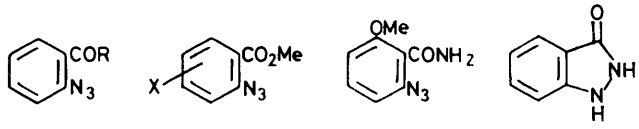
THE formation of 2-amino-3*H*-azepines by the thermolytic and photolytic decomposition of aryl azides in the presence of amines is well documented.[1-3] Reaction is thought to proceed *via* nucleophilic addition of the amine to the intermediate azirine (2), a valence tautomer of the initially formed singlet nitrene (1). Attempts to



(1) (2) (3)

extend this synthesis by carrying out aryl azide decompositions in other nucleophilic solvents (*e.g.* H_2S) [2a] have, in general, either failed or given only poor yields of 3*H*-azepine. However, photolytic decomposition of *o*-azidobenzanilides in methanol gives 2-methoxy-3*H*-azepine-3-carbanilides (3; R = NHAr, R^1 = Me, X = H) in good yield [4] and 2-methoxy-3-acetyl-3*H*-azepine (3; R = R^1 = Me, X = H) can be obtained (37%) under similar conditions from *o*-azidoacetophenone.[5] These results suggest that the carbonyl function may be promoting 3*H*-azepine formation, particularly since phenyl azide is claimed [6] to give only a poor yield (11%) of 2-methoxy-3*H*-azepine when photolysed in methanol.† We have investigated the photolysis of other azido-acid derivatives, and in a preliminary communication [7] have shown that methyl *o*-azidobenzoates undergo ring expansion to 2-alkoxy-3-methoxycarbonyl-3*H*-azepines (3; R = OMe, R^1 = Me, Et, Pr^n, Pr^i, and Bu^n, X = H) in the appropriate alcohol (R^1OH) as reaction solvent. The reaction is also applicable to the preparation of phenyl ester (3; R = OPh, R^1 = Me, X = H) and the 6-chloro-2-methoxyazepine ‡ (3; R = OMe, R^1 = Me, X = 6-Cl). We now report on the photolytic decomposition in methanol of substituted methyl *o*-azidobenzoates and other *o*-azidobenzoic acid derivatives.

Stevens and Mair [4] obtained *o*-azidobenzamides by diazotisation of the appropriate *o*-aminobenzamides followed by treatment with sodium azide. However, yields were variable and in several instances azidoamide had to be separated from the 1,2,3-benzotriazin-4-one formed in a competing reaction. In fact diazotisation of *o*-aminobenzanilide gave 3-phenyl-1,2,3-benzotriazin-4-one as the sole product. As an alternative route we prepared the hitherto unreported *o*-azidobenzoyl chloride (4; R = Cl) by treating *o*-azidobenzoic acid with thionyl chloride in dry benzene at room temperature. The acid chloride was characterised by its i.r. spectrum, and by its quantitative conversion into the known *o*-azidobenzamide with aqueous ammonia. The acid chloride with primary aromatic amines in pyridine solution gave the corresponding *o*-azidobenzanilides, and, in particular, the hitherto inaccessible *o*-azidobenzanilide (4; R = NHPh) in high yield.



(4) (5) (6) (7)

o-Azidobenzoyl chloride was also used to prepare the phenyl ester (4; R = OPh) and thioester (4; R = SPh) from phenol and thiophenol, respectively, under Schotten–Baumann conditions. *o*-Azidobenzoic anhydride (4; R = Bz) was obtained, either by treating the acid chloride (4; R = Cl) with sodium benzoate (or, conversely, benzoyl chloride with sodium *o*-azidobenzoate) in aqueous pyridine.[9] Attempts to prepare *o*-azidobenzohydrazide (4; R = $NHNH_2$) and *o*-azidobenzohydroxamic acid (4; R = NHOH) from methyl *o*-azidobenzoate led to unexpected products. For example, with an excess of cold ethanolic hydrazine hydrate the azido-ester (4; R = OMe) reacted exothermally to give the indazolinone (7) (80%), while with hydroxylamine hydrochloride in methanolic potassium hydroxide only *o*-azidobenzoic acid was obtained.[10] A

† Several attempts to reproduce this result in our laboratories have failed; only aniline and tarry products were obtained.

‡ Described in error in the preliminary communication [7] as the 7-chloro-isomer; for erratum see ref. 8.

[1] R. Huisgen, D. Vossius, and M. Appl, (*a*) *Chem. Ber.*, 1958, **91**, 1; (*b*) R. Huisgen and M. Appl, *ibid*, p. 12; (*c*) *ibid*, 1959, **92**, 2961.

[2] W. Von E. Doering and R. A. Odum, *Tetrahedron*, 1966, **22**, 81.

[3] R. J. Sundberg, S. R. Suter, and M. Brenner, *J. Amer. Chem. Soc.*, 1972, **94**, 513.

[4] A. C. Mair and M. F. G. Stevens, *J. Chem. Soc.* (*C*), 1971, 2317.

[5] M. A. Berwick, *J. Amer. Chem. Soc.*, 1971, **93**, 5780.

[6] R. J. Sundberg and R. H. Smith Jun., *J. Org. Chem.*, 1971, **36**, 295.

[7] R. K. Smalley, W. A. Strachan, and H. Suschitzky, *Synthesis*, 1974, 503.

[8] Erratum, *Synthesis*, 1976, 838.

[9] R. K. Smalley and H. Suschitzky, *J. Chem. Soc.*, 1964, 755.

[10] W. A. S. Strachan, Ph.D. Thesis, University of Salford, 1974.

similar reaction between *o*-azido-esters and *o*-azido-ketones and hydrazine hydrate has recently been reported by Rees and his co-workers.[11] The nature and scope of this intriguing indazolinone-forming reaction are currently under investigation.[12]

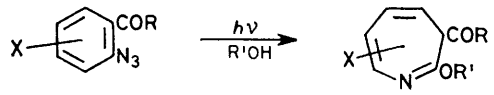
Two approaches have been employed for the synthesis of the substituted azido-esters (5); namely (a) *via* the amino-ester followed by diazotisation and azide formation or (b) *via* the azido-acid chloride and then treatment with methanol. Full details are given in the Experimental section.

The results of the photolyses are given in Table 1. The azido-amides behaved as expected and gave 3*H*-azepine-3-carboxamides (3; R = NHAr, R^1 = alkyl, X = H), the structures of which, like all the 3*H*-azepines reported in this paper, were confirmed by ^{1}H n.m.r. and mass spectral data (Table 2). As with the esters reported previously,[7] ring expansion to azepines also takes place in alcohols other than methanol.

The phenyl ester (4; R = OPh) yielded 3*H*-azepine (3; R = OPh, R^1 = Me, X = H) whereas the thio-ester (4; R = SPh) gave diphenyl disulphide as the only isolable product. *o*-Azidobenzoic anhydride (4; R = Bz) not unexpectedly gave 2-methoxy-3-methoxycarbonyl-3*H*-azepine. Obviously, methanolysis to methyl *o*-azidobenzoate had occurred during photolysis. Control experiments showed that the azido-anhydride in methanol at room temperature did, in fact, undergo slow methanolysis to give, predominantly, methyl *o*-azidobenzoate and some methyl benzoate. With aqueous ammonia only *o*-azidobenzamide was formed. Regio-

TABLE 1

Preparation of 3*H*-azepines from *o*-substituted azides



Compound number *	Azide X	Azide R	Azide R^1	3*H*-Azepine X	M.p. (°C) [b.p. (°C)/ Torr]	Yield † (%)	Found (%) C	Found (%) H	Found (%) N	Mol. formula	Required (%) C	Required (%) H	Required (%) N
(1)	H	PhNH	Me	H	159	60	69.3	5.8	11.7	$C_{14}H_{14}N_2O_2$	69.4	5.8	11.6
(2)	H	PhNH	Et	H	111	40	70.6	5.9	11.0	$C_{15}H_{16}N_2O_2$	70.6	5.9	11.0
(3)	H	*o*-MeC_6H_4NH	Et	H	150	54	71.05	6.7	10.3	$C_{16}H_{18}N_2O_2$	71.0	6.7	10.4
(4)	H	NH_2	Et	H	153	81	59.6	6.5	15.6	$C_9H_{12}N_2O$	59.9	6.5	15.5
(5)	H	NH_2	Pr^n	H	122	67	61.8	7.4	14.5	$C_{10}H_{14}N_2O$	61.9	7.3	14.4
(6)	H	OPh	Me	H	[115/0.3]	59	69.3	5.4	5.8	$C_{14}H_{13}NO_3$	69.1	5.4	5.8
	H	SPh	Me			*a*							
	H	OH	Me			*b*							
	H	OBz	Me	H		*c*							
(7)	H	OMe	Me	H		78 *d*							
(8)	H	OMe	Et	H		58 *e*							
	H	OMe	Et	H		75 *f*							
	H	OMe	Et	H		84 *g*							
	3-Cl	OMe	Me			*g,h*							
(9)	4-Cl	OMe	Me	6-Cl	40 [80/0.02]	55 *g,i*	50.2	4.7	6.5	$C_9H_{10}ClNO_3$	50.1	4.7	6.5
(10)	5-Cl	OMe	Me	5-Cl	44 [90/0.01]	40 *g*	49.8	4.6	7.3	$C_9H_{10}ClNO_3$	50.1	4.7	6.5
	6-Cl	OMe	Me			*g,j*							
(11)	4-MeO	OMe	Me	6-MeO	62	59 *g*	56.5	6.3	6.95	$C_{10}H_{13}NO_4$	56.9	6.2	6.6
(12)	5-MeO	OMe	Me	5-MeO	77	9 *g,k*	57.8	6.8	5.9	$C_{10}H_{13}NO_4$	56.9	6.2	6.6
(13)	6-MeO	NH_2	Me	4-MeO	196	49 *g*	55.1	6.1	14.6	$C_9H_{12}N_2O_3$	55.1	6.2	14.3
(14)	5-Br	OMe	Me	5-Br	42 [90/0.02]	35 *g,l*	41.3	3.8	5.9	$C_9H_{10}BrNO_3$	41.6	3.9	5.4
	5-NO_2	OMe	Me		—	*g, m*							
	3,5-Cl_2	OMe	Me		—	*g,n*							
(15)	4-CO_2Me	OMe	Me	6-CO_2Me	[120/0.1]	66 *g*	55.6	5.6	5.7	$C_{11}H_{13}NO_5$	55.2	5.5	5.85
	6-CO_2H	OMe	Me			*g,o*							

* Refers to 3*H*-azepine. † Yields are not optimised and figures quoted refer to pure chromatographed and distilled (Kugelrohr) product.

a Diphenyl disulphide (m.p. 58 °C) obtained as sole identifiable product; photolysis time 48 h. *b* Only tars and starting material (25%). *c* 2-Methoxy-3-methoxycarbonyl-3*H*-azepine (35%) and methyl benzoate (20%) obtained; photolysis time 24 h. *d* Azido-ester (5g) in MeOH (190 ml), irradiation time 24 h; similar yield with 10 g ester in MeOH (230 ml), but photolysis time 43 h. *e* Solvent, MeOH–CH_2Cl_2; photolysis time 6 h. *f* Solvent THF–EtOH; photolysis time 3 h. *g* Azido-ester (2 g) in 50 : 50 THF–alcohol mixture; photolysis time 4 h. *h* Main product methyl 3-chloroanthranilate (28%) + azido ester (2.5%) + tar. *i* Erroneously reported in ref. 7 as the 7-chloro-isomer. *j* I.r. of oil from column characteristic of 3*H*-azepine but on distillation only tar formed. *k* Difficult to purify, possibly contaminated by traces of amino-ester. *l* Methyl 5-bromoanthranilate (11%) also isolated. *m* Products are 2,2′-bis(methoxycarbonyl)-4,4′-dinitroazobenzene (23%) (Found: C, 49.0; H, 3.0; N, 14.3. $C_{16}H_{12}N_4O_8$ requires C, 49.5; H. 3.1; N, 14.4%) + methyl 5-nitroanthranilate (22%) and azido-ester (14%). *n* Products are methyl 3,5-dichloroanthranilate (22%) + azido-ester (5%) + tar. *o* Photolysis time 8 h, only tar obtained.

[11] M. E. Peek, C. W. Rees, and R. C. Storr, *J. Chem. Soc. Perkin I*, 1974, 1260.

[12] M. A. Alkhader, M.Sc. Thesis, University of Salford, 1976.

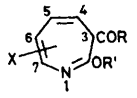
selective nucleophilic attack at the *o*-azidobenzoyl centre of the unsymmetrical anhydride is predictable as the azido-group is known to be electron withdrawing.[13a]

Monitoring of the *o*-azido-ester photolysis by i.r. spectroscopy and t.l.c. showed that azepine formation is slow in methanol solution (*ca.* 10% azide remaining after 24 h). However, it was found that reaction times could be cut drastically with no loss of yield, using a 50 : 50 methanol–dichloromethane mixture (reaction time *ca.* 8 h) and even further in 50 : 50 methanol–tetrahydrofuran (THF) solution (reaction time 3—4 h).* All subsequent azido-ester photolyses were, therefore, carried out in the latter mixture.

As can be seen from Table 1, there is no obvious correlation between yield of azepine and the nature and position of the substituent in the *o*-azido-ester. Substituents at the 3-position apparently prevent azepine formation possibly by decreasing the electron density on the carbon centre at which the electrophilic singlet nitrene attacks. The abnormally low yield of azepine from the 5-methoxy azido-ester may be a result of singlet nitrene stabilisations, (8) ⟷ (8a), which renders azirine formation less likely and allows cross-over to the lower-energy triplet nitrene. Failure of the 6-chloro-azido-ester (5; X = 6-Cl) to give azepine is not easily explained. Lack of azepine was to be expected, however, with the 5-nitro-azido-ester (5; X = 5-NO_2), since nitro-substituents are known [15] to promote intersystem crossing (singlet→triplet). Significantly, the latter azide provided the only instance of azo-compound formation in this work. Only in a few cases were *o*-amino-esters isolated and then always in minor yield (see Table 1).

TABLE 2

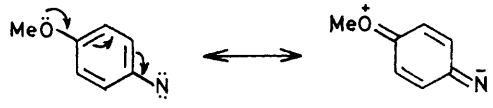
Spectral data for 3*H*-azepines



Compound number *	^{1}H N.m.r. spectra (τ) R	R^1	H-3	H-4	H-5	H-6	H-7	U.v. $\lambda_{max.}$ (log ε)	*m/e* M^+
(1)	2.2—2.8 (5 H,m)	6.25 (3 H,s)	6.54 (d) [a]	3.3—4.2 (3 H,m)			2.9—3.1 (d) [b]	256 (3.63)	242
(2)	2.0—2.7 (5 H,m)	5.5—6.0 (2 H,q) 8.6—8.8 (3 H,t)	6.3—6.4 (d) [a]	3.2—4.3 (3 H,m)			2.9—3.05 (d) [b]		256
(3)	2.1—2.8 (4 H,m)	5.6—5.9 (2 H,q) 8.7—8.95 (3 H,t)	6.1—6.25 (d) [a]	3.3—4.3 (3 H,m)			2.9—3.1 (d) [b]		270
(4)	8.3 (2 H,s)	5.5—6.0 (2 H,q) 8.7—8.9 (3 H,t)	6.5—6.6 (d) [a]	3.3—4.3 (3 H,m)			2.9—3.1 (d) [b]	255 (3.65)	180
(5)	8.1 (2 H,s)	5.9—6.2 (2 H, q) 8.0—8.7 (2 H,m) 9.0—9.3 (3 H, t)	6.5—6.7 (d) [a]	3.5—4.5 (3 H,m)			2.9—3.1 (d) [b]		194
(6)	See ref. 7								243
(7)	See ref. 7							257 (3.75)	181
(8)	See ref. 7								195
(9)	6.25 (3 H, s)	6.3 (3 H,s)	7.05 (dd) [c]	4.35 (dd) [d]	3.75 (dm) [e]		2.9 (dm) [f]	260 (3.95)	215, 217
(10)	6.31 (3 H,s)	6.32 (3 H,s)	7.05 (d) [a]	4.37 (d) [a]		4.13 (d) [b]	3.21 (d) [b]	262 (4.08)	215, 217
(11) [g]	6.25 (3 H, s)	6.30 (3 H,s)	6.71 (d) [a]	4.12 (dd) [a]	3.7 (dm) [e]		3.31 (d) [f]	264 (3.90)	211
(12) [h]	6.26 (3 H,s)	6.42 (3 H,s)	6.92 (d) [a]	5.23 (dm) [a]		4.18 (dd) [i]	3.22 (d) [b]	268 (4.09)	211
(13) [j]	3.17 (2 H,b) [k]	6.41 (3 H,s)	5.39 (d) [l]		4.1—4.6 (2 H,m)		3.48 (d) [b]	262 (3.85)	196
(14) [m]	6.34 (3 H,s)	6.36 (3 H,s)	6.96 (d) [a]	4.16 (d) [a]		3.99 (d) [b]	3.20 (d) [b]	264 (3.86)	259, 261
(15) [n]			7.0 (d) [a]	6.23 (dd) [c]	3.15 (dm) [e]		1.92 (s)	276 (3.96)	239
(16)	6.22 (3 H,s)	8.1—8.9 (10 H,m)	7.1 (d) [a]	3.4—4.5 (3 H,m)			3.1 (d) [b]		249

* See Table 1.

[a] $J_{3,4}$ 6.5—7 Hz. [b] $J_{6,7}$ 7.5—8 Hz. [c] $J_{3,4}$ 6 Hz; $J_{3,5}$ <1 Hz. [d] $J_{4,5}$ 10 Hz; $J_{3,4}$ 6 Hz. [e] $J_{4,5}$ 10 Hz; $J_{5,7}$ and $J_{3,5}$ <1 Hz. [f] $J_{5,7}$ <1 Hz. [g] 6.13 (s, 3 H, 6-OCH_3). [h] 6.24 (s, 3 H, 5-OCH_3). [i] $J_{4,6}$ 2 Hz. [j] 6.45 (s, 3 H, 4-OCH_3). [k] Removed on deuteriation. [l] $J_{3,5} \simeq$ 2 Hz. [m] Spectrum of neat liquid. [n] 6.18 (s, 9 H, OCH_3, 3-CO_2CH_3, and 6-CO_2CH_3).



(8) (8a)

The failure of *o*-azidobenzoic acid, its 5-chloro-derivative, and the azido-monoester (5; X = 6-CO_2H)

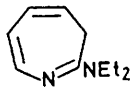
* Sundberg [14] has demonstrated the efficiency of a THF–diethylamine mixture in the preparation of 2-diethylamino-3*H*-azepines.

[13] ' The Chemistry of the Azido Group ', ed. S. Patai, Interscience Publishers, London, 1971, (*a*) p. 203; (*b*) p. 205.

[14] R. J. Sundberg and R. W. Heintzelman, *J. Org. Chem.*, 1974, **39**, 2546.

[15] R. A. Odum and A. M. Aaronson, *J. Amer. Chem. Soc.*, 1969, **91**, 5680.

to undergo ring expansion to the corresponding 3*H*-azepine deserves comment, since as far as we are aware no 3*H*-azepinecarboxylic acids have as yet been prepared. Sundberg [16] has shown that azepine formation is suppressed in acidic media, and it may be that *o*-azidobenzoic acid (K_a 29.5 × 10^{-6} at 25 °C) [13b] is sufficiently acidic to prevent ring expansion. In an effort to mask the offending acidic nature of the system a suspension of sodium *o*-azidobenzoate in methanol was photolysed. However, even after prolonged irradiation (72 h) the



(9)

azide was recovered. A similar result was obtained with a solution of the sodium salt in aqueous methanol. As an alternative approach *o*-azidobenzoic acid was photolysed in a 50 : 50 mixture of diethylamine and tetrahydrofuran, whereupon only 2-diethylamino-3*H*-azepine (9) was isolated. Whether decarboxylation takes place before or after azepine formation is not yet known.

The presence of an electron-withdrawing carbonyl substituent is apparently necessary for azepine formation, since phenyl azide, *o*-tolyl azide, *o*-azidobenzyl alcohol, and *o*-azidobenzyl methyl ether all fail to undergo ring expansion when photolysed in methanol–THF solution.[17] The carbonyl function appears to be most efficient when *ortho* to the azide group, since methyl *m*- and *p*-azidobenzoate on photolysis in methanol–THF solution give 3*H*-azepines but much more slowly (35 h and 22 h, respectively) in lesser yield, and accompanied by amino-ester and some tar.[17] Possibly for azepine formation the nitrene has to be reasonably electrophilic, a condition fulfilled most effectively by an *ortho*-positioned electron-withdrawing carbonyl group. Further work on the effect of the nature and position of the substituent on 2-alkoxy-3*H*-azepine formation is in progress.

The ease of photolytic ring expansion of azido-esters in alcoholic media led us to investigate the thermal decomposition of methyl *o*-azidobenzoate in similar solvents. Thermolysis of phenyl azide in cyclohexanol gave as in the photolytic reaction no 3*H*-azepine. Azobenzene (10%) and aniline (30%) were the only products. In contrast thermolysis of methyl *o*-azidobenzoate in boiling cyclohexanol gave a mixture of 2-cyclohexyloxy-3-methoxycarbonyl-3*H*-azepine (20%) and methyl anthranilate (60%). Thermolysis of the azido-ester under pressure in methanol at 150 °C gave a mixture, separable with difficulty of 3*H*-azepine (20%) and methyl anthranilate (14%), and much tar. Obviously thermal decomposition favours triplet-derived products, and is inferior to photolysis as a synthetic method for 2-alkoxy-3*H*-azepines. As expected, thermolysis of methyl *o*-azidobenzoate in *m*-cresol gave only aniline (40%) and tar. The acidic nature of the medium as already discussed, is probably responsible for the absence of 3*H*-azepine.

* For details of the Supplementary publication scheme, see Notices to Authors No. 7, *J.C.S. Perkin I*, 1977, Index issue.

EXPERIMENTAL

I.r. spectra were recorded as Nujol mulls of liquid films on either a Perkin-Elmer 297 or 257 grating infrared spectrophotometer. ^{1}H N.m.r. spectra were measured, unless otherwise stated for $CDCl_3$ solutions ($SiMe_4$ as internal standard) on a Varian EM-360 or a Perkin-Elmer R32 n.m.r. spectrometer. Mass spectra were obtained on an A.E.I. MS12 mass spectrometer, and u.v. spectra as ethanol solutions on a Unicam SP 800A spectrophotometer. The THF used in the photolyses was dried over $MgSO_4$ and then sodium wire and finally distilled under nitrogen from sodium and benzophenone. All m.p.s are uncorrected and distillation of all liquid samples was performed using a Kugelrohr. T.l.c. was on alumina G (type E), whereas column chromatography was carried out on alumina (type H).

Preparations.—The preparation of *o*-azidobenzoyl chloride, *N*-(*o*-azidobenzoyl)-aniline and -*o*-toluidine, phenyl *o*-azidobenzoate, *S*-(*o*-azidobenzoyl)thiophenol, *o*-azidobenzoic anhydride, methyl *o*-azidobenzoate, methyl 2-azido-3-chlorobenzoate, 2-azido-3-chlorobenzoic acid, methyl 2-azido-4-chlorobenzoate, 2-azido-4-chlorobenzoic acid, methyl 2-azido-5-chlorobenzoate, methyl 2-azido-6-chlorobenzoate, methyl 2-azido-3,5-dichlorobenzoate, 2-azido-3,5-dichlorobenzoic acid, methyl 2-azido-4-methoxybenzoate, methyl 4-methoxy-2-nitrobenzoate, methyl 2-azido-5-methoxybenzoate, 2-azido-5-methoxybenzoic acid, 2-azido-6-methoxybenzamide, 2-amino-6-methoxybenzamide, methyl 2-azido-5-bromobenzoate, methyl 2-azido-5-nitrobenzoate, dimethyl 2-azidoterephthalate, 3-azido-2-methoxycarbonylbenzoic acid, and 3-amino-2-methoxycarbonylbenzoic acid are given in Supplementary Publication No. SUP 22183 (11 pp.).*

Photolysis of o-*Azido-esters.—General procedure.* A solution of the *o*-azido-ester (2 g) in methanol (95 ml) and sodium-dried THF (95 ml) was photolysed (110 W medium-pressure lamp with Pyrex filter) in a Hanovia photochemical reactor under nitrogen. The reaction was monitored by observing the rate of disappearance of the $\nu(N_3)$ at 2 140 cm^{-1}. Reaction times were generally in the region of 3—5 h (see Table 1). When reaction was complete, the solvent was removed *in vacuo* and the brown residual oil chromatographed on alumina. Elution with light petroleum (b.p. 60—80 °C)–benzene (7 : 3) gave in some instances unchanged azido-ester (*ca.* 0.1 g) while elution with benzene gave the 2-alkoxy-3-alkoxycarbonyl-3*H*-azepines, generally as pale yellow oils, which were purified by vacuum distillation in a Kugelrohr. For physical and spectral data see Tables 1 and 2.

Further elution of the column with ethyl acetate gave, in some instances, *o*-amino-ester, while final elution with ethanol gave in all cases only intractable tars. For methyl 2-azido-3,5-dichloro- and methyl 2-azido-3-chloro-benzoate elution with benzene gave the respective amino-ester. The 2-amino-5-nitro-ester was obtained using chloroform as eluant.

The *o*-azido-amides and -anilides were photolysed under similar conditions, to give the 2-alkoxy-3*H*-azepine-3-

[16] R. J. Sundberg and K. B. Sloan, *J. Org. Chem.*, 1973, **38**, 2052.

[17] R. Purvis, R. K. Smalley, and H. Suschitzky, University of Salford, unpublished results.

carboxamides as readily crystallisable solids. For results and data see Tables 1 and 2.

Photolysis of o-*azidobenzoic acid in THF-diethylamine.* 2-Azidobenzoic acid (2 g) in a solution of diethylamine (95 ml) and dry THF (95 ml) was photolysed (110 W mercury lamp, Pyrex filter) for 24 h. Some polymer was formed and deposited on the face of the light tube which had to be cleaned at intervals during the reaction. The reaction mixture was evaporated to dryness, the residue absorbed onto alumina and chromatographed. Elution with ethyl acetate gave azepine-containing fractions which on evaporation and distillation yielded 2-diethylamino-3*H*-azepine (0.59 g, 30%) as a yellow oil, b.p. 85 °C at 1 Torr. I.r. and ^{1}H n.m.r. were identical with an authentic sample prepared by the method of Odum and Doering.[2]

Thermolysis of Phenyl Azide in Cyclohexanol.—A solution of phenyl azide (3 g) in cyclohexanol (30 ml) was heated under reflux for 3 h. The solvent was removed under pressure and the dark residual oil absorbed onto alumina and chromatographed. Elution with light petroleum (b.p. 40—60 °C) gave azobenzene, m.p. 68 °C (0.46 g, 10%) and further elution with diethyl ether gave aniline (0.73 g, 30%). Finally, elution of the column with diethyl ether–methanol (19 : 1) and then methanol gave only tarry material.

Thermolysis of methyl o-*azidobenzoate in cyclohexanol.* A solution of methyl *o*-azidobenzoate (3 g) in cyclohexanol (30 ml) was heated under reflux at 140 °C for 6 h. Treatment of the reaction mixture as in the previous experiment and chromatographic separation on alumina gave the following products. With light petroleum (b.p. 60—80 °C) as eluant, 2-*cyclohexyloxy*-3-*methoxycarbonyl*-3H-*azepine* (0.84 g, 20%), b.p. 127 °C at 0.1 Torr (Found: C, 67.5; H, 7.3; N, 5.8. $C_{14}H_{19}NO_3$ requires C, 67.4; H, 7.6; N, 5.6%). For spectral data see Table 2, compound (16).

Elution with diethyl ether yielded methyl anthranilate (1.54 g, 60%), while further elution with methanol gave only tar.

Thermolysis of methyl o-*azidobenzoate in methanol.* A solution of methyl *o*-azidobenzoate (15 g, 0.1 mol) in methanol (150 ml) was heated in a stainless-steel autoclave under dry nitrogen at 150 °C for 4 h. The reaction mixture was allowed to cool, then evaporated to dryness at reduced pressure. The residual oil distilled at 130—155 °C as a pale yellow oil (5.7 g) leaving much tarry residue. T.l.c. investigation showed the distillate to be a mixture of methyl anthranilate and 2-methoxy-3-methoxycarbonyl-3*H*-azepine separation of which proved to be very difficult. A ^{1}H n.m.r. spectrum, however, showed the oil to be a 7 : 10 mixture of amino-ester and 3*H*-azepine.

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