3*H*-Azepines and Related Systems Part 3.[1] Mono- and Bis- 2-Alkoxy-3*H*-azepine-3-carboxylates and -3-carboxamides by Photolysis of Mono- and Di- *o*-Azidobenzoyl Derivatives of Glycols and Diamines. Some Acyclic Crown Ether Analogues.

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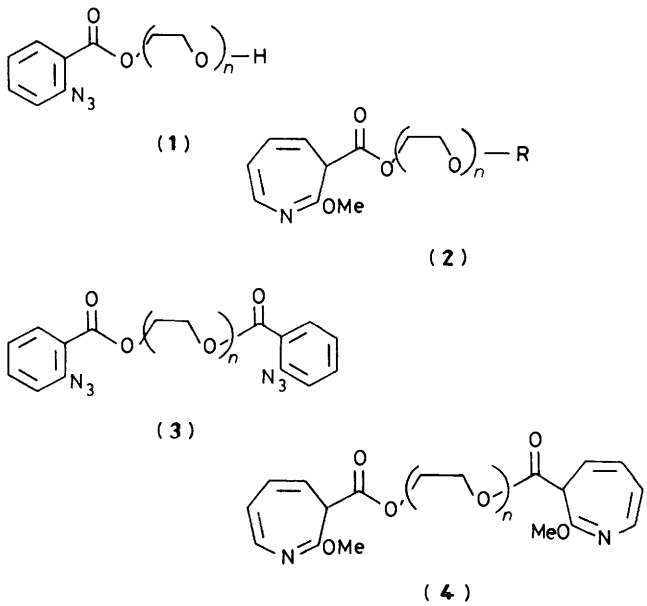
The mono-*o*-azidobenzoates (**1a**—**c**) of mono-, di-, and tri-ethylene glycol, on photolysis in methanol–tetrahydrofuran, yield the corresponding glycol monoesters (**2a**—**c**; R = H) of 2-methoxy-3*H*-azepine-3-carboxylic acid. A bis-3*H*-azepine-3-carboxylate (**4a**) is obtained from ethylene glycol di-*o*-azidobenzoate (**3a**). Similarly, bis-3*H*-azepine-3-carboxamides (**12**)—(**14**) are obtained by ring-expansion of the di-*o*-azidobenzoyl derivatives of ethylene, and *o*- and *p*-phenylene diamines. Photolysis of the *o*-azidobenzoates of 2-ethoxyethanol (**6a**) and diethylene glycol monomethyl ether (**6b**) in mono- or di-ethylene glycol, or their monoalkyl ethers and tetrahydrofuran, produces 2-alkoxy-3*H*-azepine-3-carboxylates (**5a**), (**5b**), (**7**), and (**8**) one of which, (**8**), has metal cation complexing properties. Irradiation of β-hydroxyethyl *o*-azidobenzoate (**1a**) in tetrahydrofuran furnishes a diazepino 14-crown-4 analogue (**18**), whereas on spray pyrolysis indazolo[2,1-*a*]indazole-6,12-dione (**20**) is obtained.

The thermally and photolytically induced ring-expansions of aryl azides to 2-substituted 3*H*-azepines in the presence of amines is well-documented.[2] However, ring-expansion in other nucleophilic solvents is less common, and with alcohols is effective only with an electron-withdrawing group in the aromatic nucleus, preferably at the *ortho* position to the azide function.[3,4] These reactions have been exploited[3–6] for the preparation in practicable yields of 2-alkoxy-3*H*-azepines bearing a variety of electron-withdrawing groups (*e.g.*, CO_2R, CN, CF_3, CONHAr, and SO_2NHAr). An extension of this simple and efficient process is now reported which allows the preparation of novel bis-3*H*-azepine-3-carboxylates (**4**) and -3-carboxamides (**12**)—(**14**), and some dipodands[7] (**7**) and (**8**) based on 2-alkoxy-3*H*-azepine-3-carboxylates.

o-Azidobenzoylation of mono-, di-, and tri-ethylene glycol in pyridine solution produced a mixture of the mono- and di-*o*-azidobenzoates (**1a**—**c**) and (**3a**—**c**) respectively, which were readily separated from each other by column chromatography. However, in the majority of cases an analytically pure sample could not be obtained, since separation from high boiling glycol impurities was hampered by the instability (heat and light) of the azido-esters. The esters were, however, characterised satisfactorily by spectral data (i.r., mass, and ^1H n.m.r. spectroscopy), and, on photolysis in a mixture of methanol–tetrahydrofuran (1:1) ring-expanded to give the 2-methoxy-3*H*-azepine-3-carboxylates (**2a**—**c**; R = H). The yield of azepine decreased noticeably with increasing chain length of the glycol, and again the products proved to be difficult to separate from unidentified aliphatic by-products.

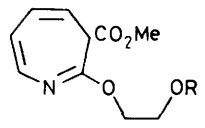
Of greater interest was the photolysis, under similar conditions, of the ethylene glycol di-*o*-azidobenzoate (**3a**), which furnished the bis-azepine-3-carboxylate (**4a**) in moderate yield (25%). Unfortunately, attempts to extend this novel double ring-expansion process to the corresponding di- and tri-ethylene glycol derivatives (**3b**) and (**3c**) failed. Photolyses in methanol–tetrahydrofuran gave only resinous products. An alternative route to the bis-azepine (**4b**) involving photolysis of the *o*-azidobenzoyl derivative (**2b**; R = *o*-$N_3C_6H_4CO$) was also unsuccessful. We were disappointed at these failures since the bis-azepine carboxylates (**4**), particularly that derived from



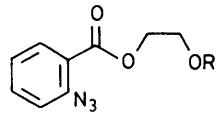
triethylene glycol, *i.e.* (**4c**), have structural features of open-chain crown ethers (podands[7]) and as such may well show metal cation complexing properties.

In an attempt to produce this type of structure, an alternative approach was adopted in which the glycol moiety was introduced into the ester and the 2-alkoxy function of the 3*H*-azepine-3-carboxylate. It has been demonstrated[1] that methyl *o*-azidobenzoate undergoes ring-expansion to 2-alkoxy-3*H*-azepine-3-carboxylates in a variety of alcohols. In ethoxyethanol and in diethylene glycol–tetrahydrofuran solution, the azido-ester ring expands in a like manner to give the azepines (**5a**) and (**5b**) respectively, in 60—70% yield.

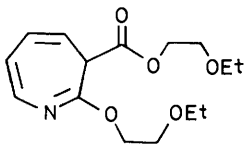
Accordingly, the ethoxyethanol and the monomethyl ethylene glycol *o*-azidobenzoates (**6a**) and (**6b**) were photolysed



(5a); R = Et
b ; R = $(CH_2)_2OH$



(6a); R = Et
b ; R = $(CH_2)_2OMe$



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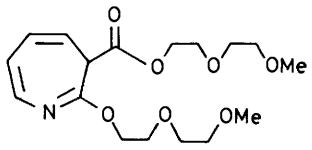
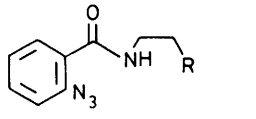


(8)

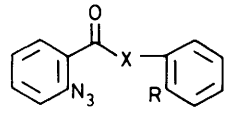
in their respective alcohols with tetrahydrofuran as co-solvent, to give the dipodands (**7**) and (**8**) respectively (50—56%) in which the 3*H*-azepine ring serves as the anchoring group.

The cation complexing abilities of azepines (**7**) and (**8**) were compared qualitatively with 15-crown-5 in the recently described[8] 'dissolution in toluene' and the '1,3,5-trinitrobenzene–Meisenheimer complex colour' tests. The ester (**7**) gave negative results with a range of cations in both tests whereas with the monomethyl ethylene glycol derivative (**8**), encouraging positive reactions were noted, particularly with lithium and potassium and, to a lesser extent, with barium and calcium cations. Further studies in this area are continuing and will be reported elsewhere.

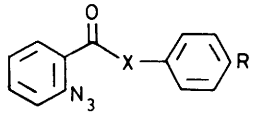
The success of the double ring-expansion of the bis-azidobenzoate (**3a**) to the bis-3*H*-azepine-3-carboxylate (**4a**) prompted a study of the photo-induced ring-expansion of bis-*o*-azidobenzoyl derivatives of other suitable bifunctional compounds. Initial results were discouraging in that the mono- and di-*o*-azidobenzoyl derivatives of ethanolamine (**9a**) and (**9b**), *o*- (**10a**) and (**10e**) and *p*-aminophenol (**11b**), pyrocatechol (**10b**) and (**10c**), hydroquinone (**11a**) and (**11c**), and *o*-aminothiophenol (**10f**) gave mainly tarry products along with small amounts of the corresponding triplet-nitrene derived amino-esters or amides. Previously,[3] difficulties have been encountered in preparing 3*H*-azepines in the presence of acidic groups, *e.g.* phenols.



(9a); R = OH
b ; R = o-$N_3C_6H_4CO_2$–
c ; R = o-$N_3C_6H_4CONH$–

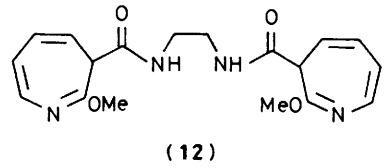


(10a); X = NH, R = OH
b ; X = O , R = OH
c ; X = O , R = o-$N_3C_6H_4CO_2$–
d ; X = NH , R = o-$N_3C_6H_4CONH$
e ; X = NH , R = o-$N_3C_6H_4CO_2$–
f ; X = S , R = o-$N_3C_6H_4CONH$–



(11a); X = O, R = OH
b ; X = NH, R = OH
c ; X = O, R = o-$N_3C_6H_4CO_2$–
d ; X = NH, R = o-$N_3C_6H_4CONH$–

In contrast, the bis-azepines (**12**), (**13**), and (**14**) were obtained in reasonable yields (20—43%) by photolysing the ethylene diamine, and the *o*- and *p*-phenylene diamine derivatives (**9c**), (**10d**), and (**11d**) respectively, in methanol–tetrahydrofuran solution.



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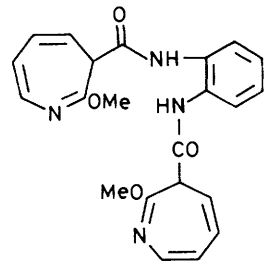

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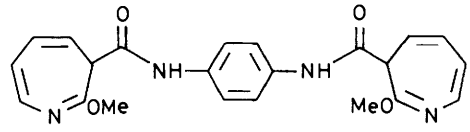
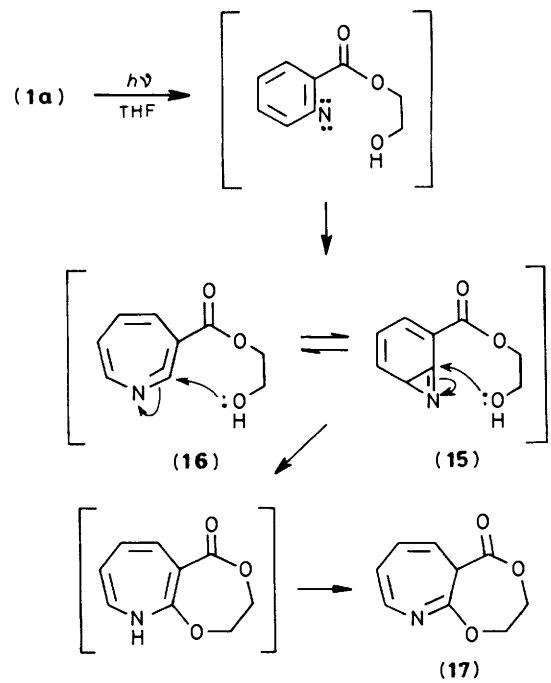


(14)

The formation of 2-substituted-3*H*-azepines by photolysis or thermolysis of aryl azides in the presence of nucleophiles is considered to involve nucleophilic attack at the reactive imine bond of either a benzazirine (**15**) or azacycloheptatetraene (**16**) intermediate* (Scheme 1). As far as we are aware, intramolecular trapping of this intermediate by a suitably placed nucleophile has not been reported. Hence, decompositions of the ethylene glycol derivative (**1a**) were carried out in the hope that nucleophilic attack by the pendant hydroxyl group would trap the intermediate (**15**) or (**16**) to yield, ultimately, the fused 7:7 heterocyclic system (**17**).

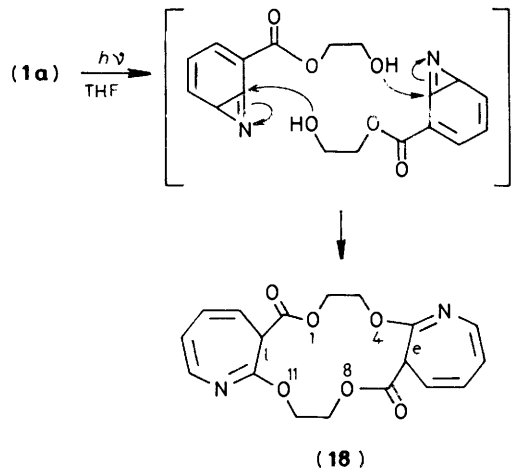


Scheme 1.

* Although spectroscopic evidence for both species is available,[10] the actual nature of the intermediate involved in ring expansions in solution, particularly of monocyclic aryl azides, is not yet clear.

Thermolysis of the ester (**1a**) in *o*-dichlorobenzene (b.p. 178 °C), in keeping with the behaviour of more simple alkyl *o*-azidobenzoates,[9] gave only tarry material and trace amounts of amino ester. However, when photolysed in tetrahydrofuran in the absence of other nucleophiles, the ester yielded, in addition to much tar, a small amount (< 10%) of a crystalline product the mass spectrum of which indicated a molecular weight of 358, *i.e.* twice that expected for the bicycle (**17**). A structure consistent with the spectral and analytical data is the diazepinotetraoxacyclotetradecane (**18**). In the mass spectrum, a double α-fission of the ester functions accounts for the base peak at *m/z* 179 units, whereas additional fragments at *m/z* 135 (15.2%) and 107 (14.9%) are consistent with further losses of OCH_2CH_2 (44 units) and CO (28 units), respectively. Also noteworthy is the secondary splitting of the triplet ethano proton resonances and of the upfield doublet (δ 2.9), which is characteristic of the azepine 3-proton.

Formation of this novel 14-crown-4 analogue was unexpected; it presumably arises by intermolecular nucleophilic additions of the glycol side chain to an imine intermediate as exemplified in Scheme 2.

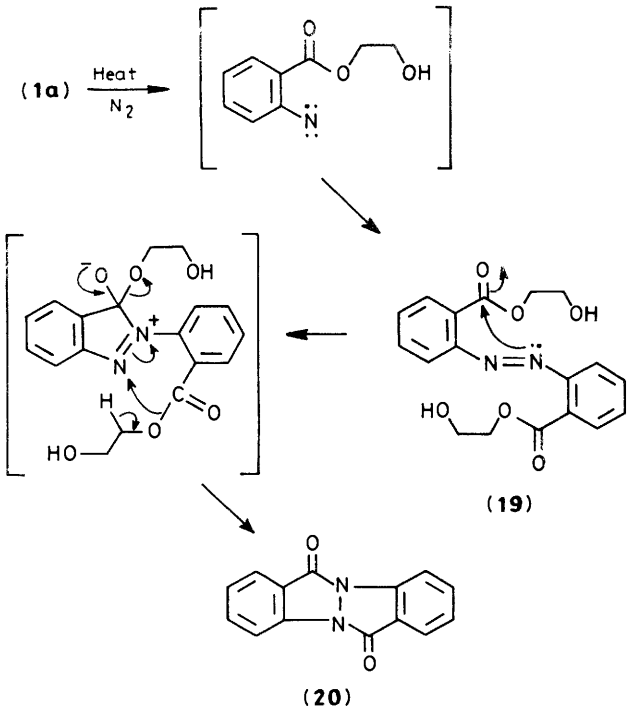


(**18**)

Scheme 2.

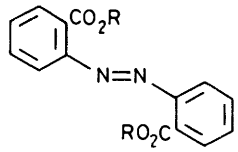
Lithium cations are known[11] to act as templates for 12-crown-4 ether formation. However, attempts to improve the yield of (**18**) by irradiating the glycol ester in tetrahydrofuran in the presence of lithium thiocyanate failed. Equally disappointing were the photolyses in tetrahydrofuran of the di- and triethylene glycol esters (**1b**) and (**1c**); only resinous products were obtained.

Flash vacuum pyrolysis techniques have been used with great success for producing and trapping unusual, and in many instances, unstable thermolysis products from a wide range of systems.[12] Therefore, in a further attempt to trap intramolecularly the intermediate (**15**) or (**16**), the glycol ester (**1a**) was subjected to spray vacuum pyrolysis, a technique which has been developed recently[13] for the pyrolysis of liquid and low melting-point samples. Pyrolysis of the ester at 320 °C was messy and gave, along with much charred and resinous material, not the bicycle (**17**) but, in low yield, indazolo[2,1-*a*]-indazole-6,12-dione (**20**) as the sole identifiable product. The origin of this tetracyclic product, which, coincidentally, we have recently prepared by an alternative route,[14] is obscure. An attractive and simple reaction pathway is by a double thermally induced cyclisation of the initially formed azobenzene-dicarboxylate (**19**) as shown in Scheme 3.* In fact, the formation



Scheme 3.

of indazoloindazolinone (**20**) during the photolysis of azobenzene-2,2′-dicarboxylic acid (**21**; R = H) has been noted previously.[15] So far, however, all attempts to obtain corroborative evidence for this mechanism have failed. For example, spray pyrolysis of the methyl and ethyl esters (**21**; R = Me or Et), prepared by thermolysis in boiling *o*-dichlorobenzene of methyl and ethyl *o*-azidobenzoate respectively, gave no trace (t.l.c.) of compound (**20**).



(**21**)

Experimental

I.r. spectra were recorded as Nujol mulls or liquid films on a Perkin-Elmer 297 or 257 grating infrared spectrophotometer. ^1H and ^{13}C N.m.r. spectra were measured, unless otherwise stated, for $CDCl_3$ solutions ($SiMe_4$ as internal standard) on a Perkin-Elmer R 32 90 MHz and a Varian Associates CFT 20 spectrometer, respectively. Mass spectra were obtained on an A.E.I. MS 12 mass spectrometer, and u.v. spectra as ethanol solutions on a Unicam SP 800A spectrophotometer. The tetrahydrofuran (THF) used in the photolyses was dried ($MgSO_4$ 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). Ether refers to diethyl ether.

o-*Azidobenzoylations: General Method.*—o-*Azidobenzoylation of ethylene glycol.* Freshly prepared[3] *o*-azidobenzoyl chloride

* We thank a referee for this most interesting suggestion.

Table 1. Mono- and di- *o*-azidobenzoyl derivatives

Comp'd.	Yield (%)	M.p. (°C)	Found (%) C	H	N	Mol. formula	Required (%) C	H	N	*m/z* M^+
(**1a**)	54	[a,g]	52.3	4.3	20.15	$C_9H_9N_3O_3$	52.2	4.4	20.3	207
(**1b**)	46	[a,d]								251
(**1c**)	52	[a]								295
(**3a**)	32	74 [b,g]	54.8	3.4	23.8	$C_{16}H_{12}N_6O_4$	54.5	3.4	23.8	352
(**3b**)	24	40 [b,g]	54.5	4.6	20.9	$C_{18}H_{16}N_6O_5$	54.5	4.1	21.2	396
(**3c**)	24	[a,g]								440
(**6a**)	58	[a]								234
(**6b**)	53	[a]								265
(**9a**)	61	67 [b]	52.4	4.8	27.0	$C_9H_{10}N_4O_2$	52.4	4.85	27.1	206
(**9b**)	11	52 [b,l]	54.7	4.0	27.9	$C_{16}H_{13}N_7O_3$	54.9	4.0	27.7	351
(**9c**)	91	188 [e]	54.8	4.2	32.1	$C_{16}H_{14}N_8O_2$	54.8	4.0	32.0	
(**10a**)	83	161 [f]	61.2	3.9	22.3	$C_{13}H_{10}N_4O_2$	61.4	4.0	22.0	
(**10b**)	60	95 [b,d]	61.2	3.5	16.6	$C_{13}H_9N_3O_3$	61.2	3.5	16.5	
(**10c**)	12	111 [g,h]	60.2	2.9	20.8	$C_{20}H_{12}N_6O_4$	60.0	3.0	21.0	
(**10d**)	35	164 [c,h]	60.2	3.6	28.2	$C_{20}H_{14}N_8O_2$	60.3	3.5	28.1	
(**10e**)	79	129 [h,i]	59.9	3.3	24.5	$C_{20}H_{13}N_7O_3$	60.1	3.3	24.6	
(**10f**)	20	148 [g,h,j]	57.8	3.3	23.5	$C_{20}H_{13}N_3O_2S$	57.8	3.1	23.6	
(**11a**)	80	146 [d,f]	61.4	3.6	16.1	$C_{13}H_9N_3O_3$	61.2	3.5	16.5	
(**11b**)	85	188 [c,h]	61.4	3.8	22.4	$C_{13}H_{10}N_4O_2$	61.4	4.0	22.0	
(**11c**)	10	122 [b,g]	60.1	3.2	20.1	$C_{20}H_{12}N_6O_4$	60.0	3.0	21.0	
(**11d**)	50	205 [k]	60.0	3.2	28.1	$C_{20}H_{14}N_8O_2$	60.3	3.5	28.1	

[a] Oil. [b] Crystallised from light petroleum. [c] Eluted with $CHCl_3$–EtOH (95:5). [d] Eluted with PhMe–$CHCl_3$ (9:1). [e] Crystallised from $HOCH_2CH_2OEt$. [f] Crystallised from PhMe. [g] Eluted with PhMe. [h] Crystallised from ethanol. [i] Prepared by *o*-azidobenzoylation of (**10a**). [j] Bis(*o*-aminodiphenyl) disulphide (40%); obtained as by-product. [k] Crystallised from DMSO. [l] Prepared in excess of ethanolamine.

Table 2. Spectroscopic data for *o*-azido- esters and amides.

Comp'd.	I.r. $\nu_{max.}$	^{1}H N.m.r. (90 MHz; $CDCl_3$) Aromatics	Others
(**1a**)	3 450 (OH; 2 120 (N_3); 1 720 (CO)	7.1—8 (4 H, m)	2.8 (1 H, bs, OH), 3.9 (2 H, t, CH_2OH), 4.4 (2 H, t, CO_2CH_2)
(**1b**)	3 450 (OH); 2 130 (N_3); 1 730 (CO)	7.1—8 (4 H, m)	2.75 (1 H, bs, OH), 3.75 (6 H, m, 3 × CH_2), 4.5 (2 H, t, CO_2CH_2)
(**1c**)	3 420 (OH); 2 150 (N_3); 1 720 (CO)	7.1—8 (4 H, m)	2.7 (1 H, bs, OH), 3.5—3.9 (10 H, m, 5 × CH_2), 4.5 (2 H, t, CO_2CH_2)
(**3a**)	2 120 (N_3); 1 740 (CO)	7.05—8 (8 H, m)	4.65 (4 H, s, 2 × CH_2)
(**3b**)	2 150 (N_3); 1 720 (CO)	7.05—8 (8 H, m)	3.9 (4 H, t, CH_2OCH_2), 4.5 (4 H, t, 2 × CO_2CH_2)
(**3c**)	2 140 (N_3); 1 720 (CO)	7.05—8 (H, m)	3.8 (H, t, 2 × CH_2OCH_2), 4.5 (4 H, t, 2 × CO_2CH_2)
(**6a**)	2 120 (N_3); 1 720 (CO)	7—8 (4 H, m)	1.2 (3 H, t, CH_3), 3.6 (4 H, m, CH_2OCH_2), 4.5 (2 H, t, CO_2CH_2)
(**6b**)	2 130 (N_3); 1 720 (CO)	7—8 (4 H, m)	3.4(3H,s,OCH_3),3.65(6H,m,$CH_2O(CH_2)_2O$), 4.6 (2 H, t, CO_2CH_2)
(**9a**)	3 400—3200 (NH) and (OH); 2 125 (N_3); 1 680 (CO)	7—8.2 (4 H, m)	3.6—3.9 (4 H, m, 2 × CH_2), 4.25 (1 H, bs, OH)
(**9b**)	3 350 (NH); 2 120 (N_3); 1 680 (CO)	7.2—8.3 (8 H, m)	4.6 (2 H, t, CH_2O), 3.8 (2 H, t, CH_2N)
(**9c**)	3 350 (NH); 2 125 (N_3); 1 675 (CO)	7.2—8.3 (8 H, m)	3.9 (4 H, s, 2 × CH_2)

(14 g) was added dropwise over 15 min to a cold stirred solution of ethylene glycol (4.8 g) in pyridine (30 ml). The mixture was stirred at room temperature for 30 min and then poured into water (150 ml) and extracted with ether (2 × 50 ml). The combined extracts were washed successively with hydrochloric acid (2 × 50 ml) and water (2 × 50 ml), dried ($MgSO_4$), and evaporated to give an oily mixture which was separated by column chromatography on alumina. Elution with light petroleum (b.p. 80—100 °C)–toluene (1:1) gave *ethylene glycol bis-o-azidobenzoate* (**3a**) (4.2 g). Further elution with toluene yielded *2-hydroxyethyl o-azidobenzoate* (8.3 g) as an oil which, by ^{1}H n.m.r., was shown to be contaminated with ethylene glycol. Repeated separation on alumina gave an analytically pure sample.

o-Azidobenzoylations of di- and tri- ethylene glycols were carried out in the same manner, as were the acylations of *o*-aminothiophenol, ethanolamine, *o*- and *p*-phenylene diamines, *o*- and *p*-aminophenol, and *o*- and *p*-hydroxyphenol. Analysis figures, % yields, and other relevant data are given in Table 1. Spectroscopic data are listed in Table 2.

Photolysis of o-Azido- esters and amides in Alcohol–Tetrahydrofuran Solution: General Procedure.—A stirred solution of the azido ester or amide (1.5—2.0 g) in alcohol (150 ml)–dry

Table 3. Mono- and bis- 2-alkoxy-3*H*-azepine-3-carboxylates and -3-carboxamides

Comp'd.	Yield* (%)	B.p. (°C)/ Torr (m.p. °C)	Found (%) C	H	N	Mol. formula	Required (%) C	H	N	*m/z* M^+
(**2a**)	56[a,b]	120/0.2	57.1	6.1	6.8	$C_{10}H_{13}NO_4$	56.9	6.2	6.6	211
(**2b**)	30[a,c]	163/0.2	56.7	6.8	5.7	$C_{12}H_{17}NO_4$	56.5	6.7	5.5	255
(**2c**)	30[a,d]	179/0.2	56.7	7.1	4.7	$C_{14}H_{21}NO_6$	56.2	7.1	4.7	299
(**4a**)	39[d,e]	232/0.1	60.3	5.7	7.9	$C_{18}H_{20}N_2O_6$	60.0	5.5	7.8	360
(**5a**)	70[c,f]	130/0.4	60.7	7.3	6.3	$C_{12}H_{17}NO_4$	60.2	7.2	5.9	239
(**5b**)	60[c,f]	150/0.4	56.5	6.9	5.5	$C_{12}H_{17}NO_5$	56.4	6.7	5.5	255
(**7**)	56[d,g]	140/0.4	60.6	7.7	5.2	$C_{15}H_{23}NO_5$	60.6	7.8	4.7	297
(**8**)	50[f,h]	170/0.4	57.4	7.9	3.7	$C_{17}H_{27}NO_7$	57.1	7.6	3.9	357
(**12**)	43[d,i]	(209)[j]	60.3	6.0	15.7	$C_{18}H_{22}N_4O_4$	60.3	6.2	15.6	358
(**13**)	39[c,i,k]	(85)[l]	64.8	5.3	14.1	$C_{22}H_{22}N_4O_4$	65.0	5.5	13.8	406
(**14**)	20[c,k,m]	(246)[n]	65.0	5.4	13.6	$C_{22}H_{22}N_4O_4$	65.0	5.5	13.8	406

* Yields are not optimised and figures cited refer to pure chromatographed and distilled (Kugelrohr), or crystallised, product. [a] Eluted with PhMe–$CHCl_3$ (9:1). [b] Irradiation time 4 h. [c] Irradiation time 8 h. [d] Irradiation time 10 h. [e] Eluted with PhMe. [f] Eluted with light petroleum–EtOAc (9:1). [g] Eluted with light petroleum–EtOAc (1:1). [h] Irradiation time 12 h. [i] Eluted with $CHCl_3$. [j] Crystallised from EtOH. [k] Small amount of amino ester also obtained. [l] Crystallised from light petroleum–PhMe. [m] Eluted with $CHCl_3$–EtOH (9:1). [n] Crystallised from light petroleum (b.p. 100—120 °C).

Table 4. ^{1}H N.m.r. data for mono- and bis- 2-alkoxy-3*H*-azepine-3-carboxylates and -3-carboxamides

Comp'd.	Azepine ring(s) 3-H	4-H	5-H	6-H	7-H	2-Substituent	Others
(**2a**)	3.1 (d)	5.65 (dd)	6.27 (m)	6.08 (dd)	7.0 (d)	3.75 (3 H, s, OMe)	4.3 (2 H, t, CO_2CH_2), 3.8 (2 H, t, CH_2OH), 3.0 (1 H, brs, OH)
(**2b**)	3.13 (d)	5.67 (dd)	6.26 (m)	6.05 (dd)	7.0 (d)	3.73 (3 H, s, OMe)	4.4 (2 H, t, CO_2CH_2), 3.7 (6 H, m, 3 × CH_2), 2.85 (1 H, brs, OH)
(**2c**)	3.13 (d)	5.67 (dd)	6.3 (m)	6.07 (dd)	7.0 (d)	3.75 (3 H, s, OMe)	4.4 (2 H, t, CO_2CH_2), 3.7 (10 H, m, 5 × CH_2), 2.7 (1 H, brs, OH)
(**4a**)	3.1 (d)	5.67 (dd)	6.32 (dd)	6.08 (dd)	7.0 (d)	3.75 (6 H, s, 2 × OMe)	4.47 (4 H, s, 2 × CH_2)
(**5a**)	3.1 (d)	5.7 (dd)	6.4 (m)	6.2 (dd)	7.0 (d)	1.1 (3 H, t, CH_2CH_3), 3.6 (4 H, m, CH_2OCH_2), 4.3 (2 H, t, CH_2)	3.8 (3 H, s, CO_2Me)
(**5b**)	3.1 (d)	5.7 (dd)	6.4 (m)	6.2 (dd)	6.9 (d)	2.8 (1 H, br, OH), 3.6 (6 H, m, 3 × CH_2), 4.3 (2 H, m, OCH_2)	3.8 (3 H, s, CO_2Me)
(**7**)	3.2 (d)	5.7 (dd)	6.4 (m)	6.1 (dd)	7.0 (d)	*a*	*a*
(**8**)	3.1 (d)		5.5—6.5 (m)		7.0 (d)	*b*	*b*
(**12**)	3.32 3.38 (d)	5.63 (dd)	6.4 (dd)	6.0 (dd)	6.95 (d)	3.71 (6 H, s, 2 × OMe)	3.35 (4 H, s, 2 × CH_2), 6.4 (2 H, br, 2 × NH)
(**13**)	3.4 3.25 (d)	5.65 (dd)	6.39 (dd)	6.0 (dd)	6.93 (d)	3.69 (3 H, s, OMe), 3.62 (3 H, s, OMe)	7—7.6 (4 H, m, ArH), 8.4 (2 H, br, 2 × NH)
(**14**)	2.95 (d)	5.77 (dd)	6.32 (dd)	6.09 (dd)	7.0 (d)	3.68 (3 H, s, OMe), 3.6 (3 H, s, OMe)	7.5—7.8 (4 H, m, ArH), 9.95 (2 H, br, 2 × NH)

[a] 1.2 (6 H, overlapping triplets, 2 × CH_2CH_3), 3.6 (8 H, m, 4 × CH_2), 4.3 (4 H, overlapping triplets, 2 × CH_2); [b] 3.4 (6 H, s, 2 × CH_3), 3.6 (12 H, m, 6 × CH_2), 4.3 (4 H, m, 2 × CH_2).

tetrahydrofuran (150 ml) was photolysed (400 W medium pressure lamp with a Pyrex filter) in a water-cooled photochemical reactor under nitrogen, until the azide [as shown by the disappearance of $\nu(N_3)$ at *ca.* 2 120 cm^{-1}] had decomposed (see Table 3 for irradiation times). The solvent was removed from the mixture under reduced pressure (rotary evaporator) and the oily or semi-solid residue chromatographed on alumina.

Products were purified further either by crystallisation or by distillation (bulb-to-bulb) under reduced pressure; see Table 3 for details.

Bis-*o*-azido -benzoates and -benzamides were treated in a similar manner. Physical data and analyses are given in Table 3, whereas n.m.r. spectroscopic data are shown in Tables 4 and 5.

Photolysis of β-*Hydroxyethyl* o-*Azidobenzoate* (**1a**) *in Tetrahydrofuran.*—A solution of β-hydroxyethyl *o*-azidobenzoate (2 g) in dry tetrahydrofuran (300 ml) was irradiated under the conditions outlined in the general method for 15 h. Evaporation of the solvent from the reaction mixture yielded an oily residue which was chromatographed on an alumina column. Elution with toluene–chloroform (9:1, v/v) gave *bis*-3H-*azepino*[2,3-

Table 5. ^{13}C N.m.r. spectroscopic data for 2-alkoxy-3*H*-azepine-3-carboxylates

Comp'd.	Azepine ring 2-C	3-C	4-C	5-C	6-C	7-C	C=O	Others
(**2a**)	146 (s)	49.2 (d)	114.8 (d)	126.2 (d)	116 (d)	136.3 (d)	168.3 (s)	66.3 and 60.05 (2 × CH_2), 55.0 (q, OCH_3)
(**2b**)	145.8 (s)	48.9 (d)	114.5 (d)	126 (d)	115.7 (d)	136.3 (d)	167.8 (s)	71.9, 68.2, 63.8, and 60.8 (4 × CH_2), 54.7 (q, OCH_3)
(**2c**)	146.2 (s)	49.4 (d)	115 (d)	126.4 (d)	116 (d)	136.7 (d)	168.4 (s)	70.4, 70.2, 68.7, 64.2, 61.5, and 55.2 (6 × CH_2), 55.15 (q, OCH_3)
(**5b**)	145 (s)	49.2 (d)	114.4 (d)	126.05 (d)	116 (d)	136.3 (d)	168 (s)	67.4, 66.9, 65.8 (3 × CH_2), 51.4 (q, OCH_3), 14.5 (q, CH_3)
(**8**)	144.6 (s)	48.9 (d)	114.1 (d)	125.7 (d)	115.6 (d)	136.1 (d)	167.2 (s)	71.1, 69.6, 68.0, 66.5, and 63.5 (8 × CH_2), 57.85 (q, 2 × OCH_3)

Table 6. Complexation tests of dipodands with metal cations

Test Comp'd./ Metal ion[a] test	Li^+ I[d]	Li^+ II[f]	Na^+ I[b]	Na^+ II[e]	NH_4^+ I[d]	NH_4^+ II[e]	K^+ I[b]	K^+ II[e]	Ca^{2+} I[c]	Ca^{2+} II[f]	Ba^{2+} I[d]	Ba^{2+} II[f]
15-Crown-5	+++[g]	++	++	++	—	++	++	++	+	++	+++	++
(**7**)	—	—	—	—	—	—	—	—	—	—	—	—
(**8**)	+++	++	+	—	—	+	+++	++	+	—	++	—

[a] Salts used were [b] bromide, [c] chloride, [d] iodide, [e] carbonate, and [f] hydroxide; [g] +++ represents an immediate positive test; ++ a positive test after 1 h; and + a slow (>12 h) positive test.

e:2′,3′-l]-1,4,8-11-*tetraoxacyclotetradecane*-6,16-*dione* (**18**) (0.2 g) as a white solid which crystallised from toluene, m.p. 225 °C (Found: C, 60.2; H, 5.3; N, 7.75. $C_{18}H_{18}N_2O_6$ requires C, 60.3; H, 5.1; N, 7.8%); $\nu_{max.}$(Nujol) 1 740 (CO) and 1 620 (CN) cm^{-1}; δ_H {90 MHz, $CDCl_3$–[$(CD_3)_2SO$]} 3.85—3.90 (2 H, overlapping d, 3- and 3′-H), 3.9—4.3 (4 H, m, 2 × CH_2), 4.55—4.95 (4 H, m, 2 × CH_2), 5.65—5.75 (2 H, overlapping d, 4- and 4′-H), 6.0—6.45 (4 H, m, 5-, 6-, 5′- and 6′-H), 7.0 (2 H, d, 7- and 7′-H); δ_C {29.2 MHz, $CDCl_3$–[$(CD_3)_2SO$]}, 48.8 (d, C-3), 62.7 (t, CH_2), 65.0 (t, CH_2), 115.3 (d, C-4), 116.2 (d, C-6), 125.9 (d, C-5), 136.6 (d, C-7), 144.7 (s, C-2), 168.0 (s, CO); *m/z* 358 (M^+), 179 (M − 179)$^+$ (100%), 135 (15), 107 (15), 91 (18), 80 (19), and 79 (39.7).

Spray Pyrolysis of 2-Hydroxyethyl o-Azidobenzoate.—2-Hydroxyethyl *o*-azidobenzoate (2.8 g) was subjected to spray vacuum pyrolysis in the apparatus described.[13] The azido ester was admitted into the pyrolysis tube, which was packed with glass beads, and maintained at 320 °C and 0.8 Torr, over a period of 2 h. After completion of pyrolysis, the pyrolysate, collected on the liquid nitrogen cooled cold-finger trap, was allowed to warm to room temperature and then washed, along with the pyrolysis tube, with dichloromethane. Evaporation of the washings gave a black tarry residue which was pre-adsorbed onto alumina and chromatographed (medium pressure column). Elution with light petroleum (b.p. 60—80 °C)–ethyl acetate (7:3 v/v) gave indazolo[2,1-*a*]-indazole-6,12-dione (**20**) (0.1 g; 5%), m.p. 298 °C (identical in all respects with an authentic sample)[14] as the sole identifiable product. Further elution of the column with a variety of solvents gave only tarry fractions.

Complexation Tests of Dipodands (**7**) *and* (**8**) *with Metal Cations.*—These tests were carried out as directed in reference 8 and the results are given in Table 6.

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