Substituted Bicyclic and Tricyclic Oxazolo[4,5-*d*]-1,2,3-Triazole Systems: Ring Expansions to 1,3,4,5-Oxatriazines and Ring Contractions to 1,2,3-Triazaspiroalkane Derivatives

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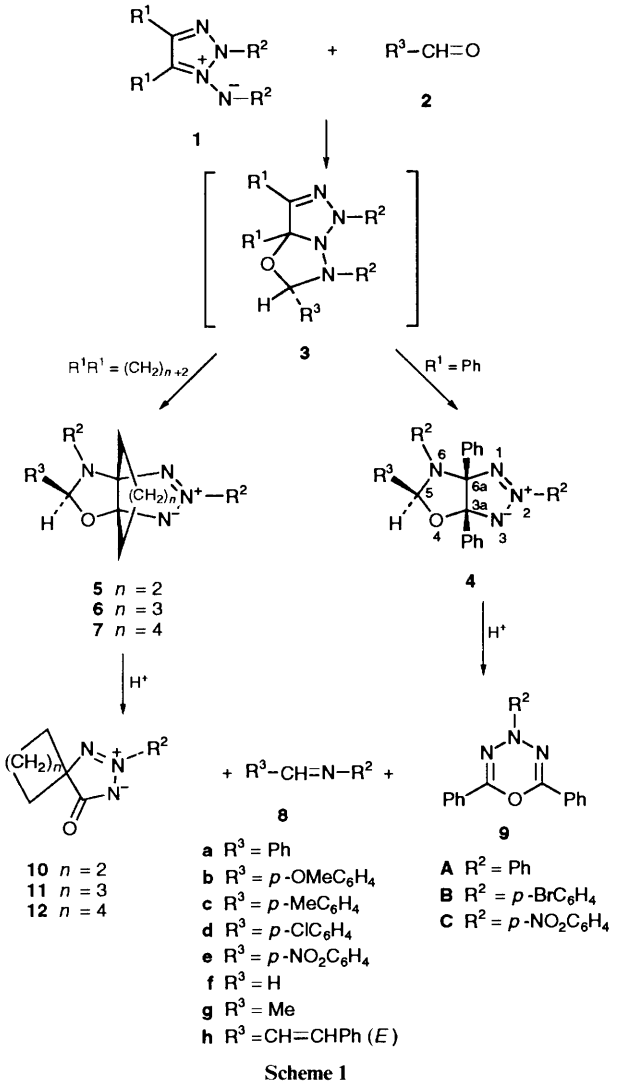
Synthesis of a range of new bicyclic and tricyclic fused oxazolo[4,5-*d*]-1,2,3-triazole systems is described. Treatment of these with acid caused transformations to substituted 1,3,4,5-oxatriazine and new 1,2,3-triazaspiroalkane systems which were isolated in high yields. Kinetic studies of the ring transformations indicated the presence of a delocalised carbocation intermediate and the mechanism of the ring expansion and contraction is discussed.

Among the azapentalene systems the fused oxazolo-1,2,3-triazole ring system was unknown[1] until we reported[2] the first example, compound **4Ah** (Scheme 1), from the reaction of the 1,2,3-triazol-1-ium-1-aminide 1,3-dipole **1** (R^1 = Ph) with cinnamaldehyde where cycloadditions occurred on the aldehyde group. This reaction has been extended to a range of aldehydes and to a range of cycloalka-1,2,3-triazoliumaminides **1** [$R^1R^1 = (CH_2)_{n+2}$]. The overall reaction is an example of a general cycloaddition–rearrangement sequence displayed by 1,3-dipoles of type **1**.[3–5] It involves a cycloaddition to an unstable initial adduct **3** which undergoes an *in situ* 1,4 N→C sigmatropic rearrangement to give products **4–7** when the dipolarophile is an aldehyde. The tricyclic derivatives of the ring system **5–7** are the first examples of oxatetraazapropellane systems. Transformations are easily induced which convert these first isolated products, **4–7**, in high yields, into the rare 1,3,4,5-oxatriazine systems **9** and new 1,2,3-triazaspiroalkane derivatives **10–12**.



Scheme 1

Results and Discussion

(a) *Oxazolo*[4,5-d]-1,2,3-*triazoles: First Generation Products.*—Treatment of the dipoles **1** (R^1 = Ph) with aromatic aldehydes in dry acetone under reflux gave the products **4Aa–4Ae** in high yields (Table 1, Nos. 1–5). The reactions with acetaldehyde and formaldehyde were carried out at 70 °C in *p*-xylene with the formaldehyde being first generated by heating an excess of paraformaldehyde at 138 °C for 30 min in *p*-xylene, cooling the solution to 70 °C and introducing the dipole (Table 1, Nos. 6–11). No reactions were observed between any of the dipoles **1** and ketones such as acetone or ethyl methyl ketone. With the cycloalka-1,2,3-triazol-1-ium-1-amidines **1** [$R^1R^1 = (CH_2)_{n+2}$] care was required to avoid a benzidine-type rearrangement[6] of the substrate which was promoted by traces of carboxylic acid present in the aldehydes. In these cases a 1:1 (v/v) mixture of the aldehyde in pure acetone was used as solvent and reagent thereby providing an 80–90 fold molar excess of the aldehyde in a dry, polar non-acidic medium. This procedure proved effective and gave high yields of the tricyclic products **5–7** (Table 1, Nos. 12–18). The structures of the products **4–7** were established on the basis of microanalytical results and ^{1}H and ^{13}C NMR spectral data which showed all of the expected signals, including the key signals at the bridgehead fusion sites. We have previously established the shifts of these carbons with fused structures containing comparable bridgeheads using X-ray crystallography and ^{13}C NMR spectra.[7] We have also previously reported[2] an X-ray crystal structure of **4Ah** confirming the *exo* orientation of R^3. This is a feature of the general reaction,[3,5] *i.e.* initial *endo* cycloaddition, as in adduct **3**, which gives rise to *exo* substitution after the rearrangement to the first generation products such as **4–7**.

(b) *Substituted* 1,3,4,5-*Oxatriazines and* 1,2,3-*Triazaspirocycloalkanes: Second Generation Products.*—When the first generation products **4** were heated briefly under reflux in ethanol containing acetic acid they were converted, in high yields, into derivatives of the rare[8] 1,3,4,5-oxatriazine ring

Table 1 First generation products: oxazolo[4,5-*d*]-1,2,3-triazoles

No.	Compd.	M.p. (*T*/°C)[a]	Yield (%)	Mol. formula	Found (required) (%) C	H	N
1	**4Aa**	174–175	80	$C_{33}H_{26}N_4O$	79.9 (80.1)	5.4 (5.25)	11.3 (11.3)
2	**4Ab**	175–176	70	$C_{34}H_{28}N_4O_2$	77.6 (77.9)	5.4 (5.35)	10.9 (10.8)
3	**4Ac**	172–176	84	$C_{34}H_{28}N_4O$	80.1 (80.3)	5.6 (5.5)	10.9 (11.0)
4	**4Ad**	165–166	81	$C_{33}H_{25}ClN_4O$	75.1 (74.9)	4.8 (4.7)	10.5 (10.6)
5	**4Ae**	191–192	75	$C_{33}H_{25}N_5O_3$	73.3 (73.45)	4.5 (4.6)	12.8 (12.95)
6	**4Af**	202–203	83	$C_{27}H_{22}N_4O$	77.7 (77.5)	5.3 (5.25)	13.3 (13.4)
7	**4Bf**	195–196	68	$C_{27}H_{20}Br_2N_4O$	56.2 (56.3)	3.6 (3.5)	9.6 (9.7)
8	**4Cf**	216–217	94	$C_{22}H_{20}N_6O_5$	63.8 (63.8)	3.7 (3.9)	16.3 (16.5)
9	**4Ag**	192–193	80	$C_{28}H_{24}N_4O$	78.0 (77.8)	5.6 (5.5)	13.0 (13.0)
10	**4Bg**	191–192	71	$C_{28}H_{22}Br_2N_4O$	56.8 (56.95)	3.6 (3.75)	9.3 (9.5)
11	**4Cg**	194–195	80	$C_{28}H_{22}N_6O_5$	64.2 (64.4)	4.1 (4.2)	15.9 (16.1)
12	**5Af**	72–73	90	$C_{19}H_{20}N_4O$	71.4 (71.25)	6.4 (6.25)	17.4 (17.5)
13	**5Bf**	130–131	70	$C_{19}H_{18}Br_2N_4O$	47.6 (47.7)	3.7 (3.75)	11.5 (11.7)
14	**5Cf**	213–214	88	$C_{19}H_{18}N_6O_5$	55.5 (55.6)	4.6 (4.4)	20.5 (20.5)
15	**5Cg**	203–204	81	$C_{20}H_{20}N_6O_5$	56.8 (56.6)	4.9 (4.7)	19.8 (19.8)
16	**6Cf**	214–215	89	$C_{20}H_{20}N_6O_5$	56.9 (56.6)	4.7 (4.7)	19.5 (19.8)
17	**6Cg**	170–171	80	$C_{21}H_{22}N_6O_5$	57.4 (57.5)	4.9 (5.0)	19.0 (19.2)
18	**7Cg**	144–145	83	$C_{22}H_{24}N_6O_5$	58.4 (58.4)	5.1 (5.3)	18.7 (18.6)

[a] After recrystallisation from EtOH.

Table 2 Second generation products: 1,3,4,5-oxatriazines and triazaspiroalkanes

Compd.[a]	M.p. (*T*/°C)[b]	Yield (%)	Mol. formula	Found (required) (%) C	H	N
9A	170–171	93	$C_{20}H_{15}N_3O$	76.5 (76.7)	5.0 (4.8)	13.4 (13.4)
9B	179–180	78	$C_{20}H_{14}BrN_3O$	60.9 (61.2)	3.6 (3.6)	10.7 (10.7)
9C	224–225	85	$C_{20}H_{14}N_4O_3$	66.9 (67.0)	3.8 (3.9)	15.6 (15.65)
10A	73–75	89	$C_{12}H_{13}N_3O$	67.2 (67.0)	6.2 (6.05)	19.4 (19.5)
10B	167–168	80	$C_{12}H_{12}BrN_3O$	48.6 (49.0)	4.1 (4.1)	14.3 (14.3)
10C	209–210	95	$C_{12}H_{12}N_4O_3$	55.3 (55.35)	4.6 (4.6)	21.2 (21.5)
11C	190–191	85	$C_{13}H_{14}N_4O_3$	57.1 (56.95)	4.9 (5.1)	20.1 (20.4)
12C	161–162	81	$C_{14}H_{16}N_4O_3$	58.5 (58.35)	5.5 (5.55)	19.2 (19.4)

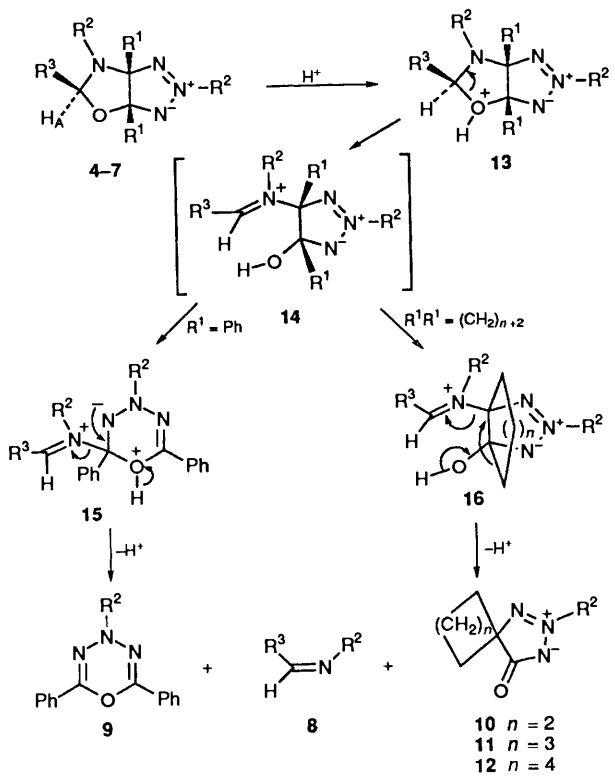
[a] Products and yields were independent of R^3. [b] After recrystallisation from EtOH.

system **9** (Table 2). The imines **8** were also liberated in this reaction but they were rapidly solvolysed under the conditions. Their presence was fully confirmed by observing the growth and disappearance of their ^1H NMR signals in the reaction solution and by comparison with signals from authentic samples under similar conditions. When the first generation products **5–7** were similarly heated in ethanol containing acetic acid the imines **8** were again extruded accompanied by a novel ring contraction which gave the triazaspiro compounds **10–12** (Table 2). For reactions carried out under reflux the nature and yields of these second generation products were not affected by the substituent R^3 and the same products in the same yields were obtained from different R^3-substituted compounds **4–7**. The structures of the products **9–12** were established on the basis of microanalytical results, IR and ^1H and ^{13}C NMR spectral data which showed all of the expected signals. Compound **9A** was identical with a known sample, previously prepared by UV irradiation of 2,4,5-triphenyl-1,2,3-triazole 1-oxide,[8] the only other known route to this oxatriazine ring system. For the compounds **10–12** the spiro carbon signal was particularly characteristic in the ^{13}C NMR spectra.

Mechanism: Kinetics.—Following extensive attempts to devise a reliable kinetic measurement of the transformation for the series **4** it was found that 270 MHz ^1H NMR spectra could be used to follow the disappearance of the H_A proton (Scheme 2, Fig. 1). The rate of product appearance could also be measured but this gave results with a scatter of 10%. The growing signal at the far left (δ 8.4) in Fig. 1 is the methine CH of **8**. This could not be used to measure rates due to concomitant hydrolysis of **8**. Rate constants were measured at 50 °C in $CDCl_3$ containing 22 mol of CD_3CO_2D per mol of **4** by following the disappearance of H_A. These were reproducible to ±2% over many runs for each compound. The rates were first-order with the following values for substrate, $k \times 10^4$ s^{-1} (Hammett σ^-_p):[9] **4b**, 3.9 (−0.26); **4c**, 2.6 (−0.17); **4a**, 2.2 (0.0); **4d**, 1.5 (0.19); **4e**, 0.08 (1.27). These values correspond to a Hammett ρ value of −1.09 (r = 0.996) and it was necessary to use the exalted resonance values for the substituents, and particularly the *p*-nitro substituent, in order to correlate the strong rate-inhibition caused by this group. Similar rate values were measured from the appearance of products **9** and there were no long-lived intermediates. The data require a cationic centre in the transition state which is strongly delocalised into R^3. We propose the mechanism outlined in Scheme 2. Rapid protonation of the oxygen leads, *via* **13**, to the key cationic species **14** in which the immonium charge is strongly delocalised into the aryl ring of R^3. This cannot happen until the C–O bond is broken and the tetrahedral carbon carrying R^3 is changed into the sp^2 imino carbon. Loss of the imine may now lead to the products **9** or **10–12**, the latter of which involves a 1,2-shift and ring-contraction in the cycloalkane.

Experimental

M.p.s were measured on an Electrothermal apparatus. IR



Scheme 2

spectra were measured with a Perkin-Elmer 983G spectrophotometer. NMR spectra were measured on a JEOL JNM-GX-270 instrument with tetramethylsilane as internal reference; J values are given in Hz. The symbols H_o, H_m and H_p refer to *ortho*-, *meta*- and *para*-protons. The substrates **1** were prepared as previously described.[7,10] Microanalyses were measured on a Perkin-Elmer model 240 CHN analyser. The following are typical examples of the reactions summarised in Tables 1 and 2.

(i) 2,3a,6,6a-*Tetraphenyl*-3a,5,6,6a-*tetrahydro*-3H-*oxazolo*-[4,5-d]-1,2,3-*triazol*-2-*ium*-3-*ide* **4Af**.—A suspension of paraformaldehyde (0.4 g) in *p*-xylene (20 cm^3) was heated under reflux for 30 min, cooled to 70 °C and treated with the triazolium compound **1** ($R^1 = R^2 = Ph$) (0.18 g, 0.46 mmol). The mixture was stirred at 70 °C for 20 min or until a clear yellow solution had developed after which excess of paraformaldehyde was filtered off and the filtrate evaporated under reduced pressure. Crystallisation of the residue from ethanol gave compound **4Af** (0.16 g, 83%), m.p. 202–203 °C (EtOH); ν_{max}(Nujol)/cm^{-1} 1598 [N=N$^+$(Ar)–N$^-$]; δ_H($CDCl_3$) 5.065 (1 H, d, J 2.3, 5-H *endo*), 5.775 (1 H, d, 5-H *exo*), 6.74–6.8 (2 H, m, ArH), 7.0–7.22 (12 H, m, ArH), 7.45–7.59 (4 H, m, ArH) and 8.34–8.37 (2 H, m, ArH); δ_C($CDCl_3$) 80.83 (C-5), 95.95 and 114.87 (C-6a and C-3a bridgeheads, respectively), 140.62, 123.03 and 132.14 (C-1′, 3-2′ and C-4′, respectively, N-2-phenyl), 136.75 (C-1′; C-6a phenyl), 137.2 (C-1′; C-3a phenyl), 142.52, 115.95 and 119.2 (C-1′, C-2′ and C-4′, respectively; N-6-phenyl), 129.04, 128.92, 128.16, 128.03, 127.78, 127.46, 127.14 and 126.83 (remaining aromatics).

(ii) 5-exo-*Methyl*-2,3a,6,6a-*tetraphenyl*-3a,6,6a-*tetrahydro*-3H-*oxazolo*[4,5-d]-1,2,3-*triazol*-2-*ium*-3-*ide* **4Ag**.—To a solution of **1** ($R^1 = R^2 = Ph$; 0.5 g, 1.28 mmol) in *p*-xylene (20 cm^3), acetaldehyde (0.35 cm, 6.36 mmol) was added and the mixture stirred and heated at 70 °C for 2 h. Evaporation of the solvent under reduced pressure and crystallisation of the residue from ethanol gave compound **4Ag** (0.44 g, 80%), m.p. 192–193 °C

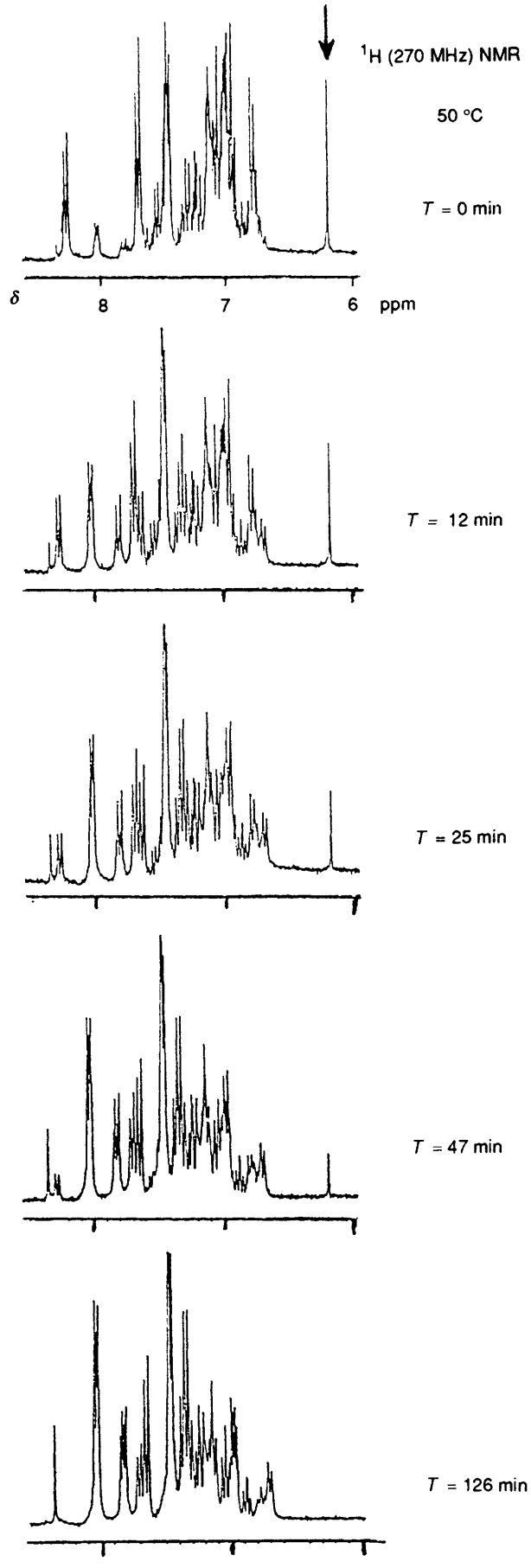


Fig. 1 Thermolysis of compound **4Ab**

(EtOH); ν_{max}(Nujol)/cm^{-1} 1600 [N=N$^+$(Ar)–N$^-$]; δ_H(CDCl$_3$) 1.70 (3 H, d, *J* 4.8, Me), 5.49 (1 H, q, 5-H), 6.7–7.4 (18 H, m, ArH) and 8.13–8.33 (2 H, m, ArH); δ_C(CDCl$_3$) 19.84 (Me), 87.35 (C-5), 98.48, 112.34 (C-6a and C-3a, respectively; bridgeheads), 140.6, 122.9, 132.0 (C-1′, C-2′ and C-4′, respectively; N-2-phenyl), 136.82 (C-1′; C-6a phenyl), 138.28 (C-1′; C-3a phenyl), 143.1, 117.4, 120.4 (C-1′, C-2′ and C-4′, respectively; N-6-phenyl) and 129.04, 128.54, 128.03, 127.71, 127.52 and 126.76 (remaining aromatics).

(iii) 2,6-*Bis*(p-*nitrophenyl*)-3a,5,6,6a-*tetrahydro*-3H-3a,6a-*pentanooxazolo*[4,5-d]-1,2,3-*triazol*-2-*ium*-3-*ide* **6Cf**.—A suspension of paraformaldehyde (0.4 g) in *p*-xylene (20 cm^3) was heated under reflux for 30 min, after which it was cooled to 70 °C and treated with compound **1C** [R^{1}R^1 = (CH$_2$)$_5$] (0.5 g, 1.27 mmol). The mixture was stirred at 70 °C for 20 min or until a clear yellow solution had formed. Excess of paraformaldehyde was filtered off and the filtrate evaporated under reduced pressure. Crystallisation of the residue from ethanol gave compound **6Cf** (0.48 g, 89%), m.p. 214–215 °C (EtOH); ν_{max}(Nujol)/cm^{-1} 1594 [N=N$^+$(Ar)–N$^-$]; δ_H(CDCl$_3$) 1.52–1.87 (6 H, m, cycloheptyl), 2.1–2.24 (4 H, m, cycloheptyl), 4.785 (1 H, d, *J* 2.2, 5-H *endo*), 5.225 (1 H, d, 5-H *exo*), 7.005 (2 H, d, J_{AB} 9.15, N(6)-*p*-NO$_2$C$_6$H$_4$, H$_o$), 8.155 (2 H, d, N(6)-*p*-NO$_2$C$_6$H$_4$, H$_m$), 8.325 (2 H, d, J_{AB} 9.5, N(2)-*p*-NO$_2$C$_6$H$_4$, H$_m$), 8.365 (2 H, d, N(2)-*p*-NO$_2$C$_6$H$_4$, H$_o$); δ_C(CDCl$_3$) 23.9, 24.1, 30.13, 30.6 and 34.4 [(CH$_2$)$_5$], 78.6 (C-5), 92.84 and 114.05 (C-6a and C-3a, respectively; bridgeheads), 139.5, 124.05, 124.36 and 149.0 (C-1′, C-2′, C-3′ and C-4′, respectively; N-2-*p*-NO$_2$C$_6$H$_4$) and 149.0, 114.05, 125.6 and 140.2 (C-1′, C-2′, C-3′ and C-4′, respectively; N-6-*p*-NO$_2$C$_6$H$_4$).

(iv) 2,6-*Bis*(p-*nitrophenyl*)-5-exo-*methyl*-3a,5,6,6a-*tetrahydro*-3H-3a,6a-*pentanooxazolo*[4,5-d]-1,2,3-*triazol*-2-*ium*-3-*ide* **6Cg**.—A solution of compound **1C** [R^1-R^1 = (CH$_2$)$_5$] (0.5 g, 1.27 mmol) in acetone (5 cm^3) was treated with acetaldehyde (5 cm^3, 0.89 mol) and the mixture was stirred at room temperature for 12 h. It was then evaporated under reduced pressure and the residue crystallised from ethanol to give compound **6Cg** (0.44 g, 80%), m.p. 170–171 °C (EtOH); ν_{max}(Nujol)/cm^{-1} 1597 [N=N$^+$(Ar)–N$^-$]; δ_H(CDCl$_3$) 1.18–1.48 (2 H, m, cycloheptyl) 1.53 (3 H, d, *J* 5.0, Me), 1.68–2.65 (8 H, m, cycloheptyl) 5.205 (1 H, q, 5-H), 7.075 (2 H, d, J_{AB} 9.1, N(6)-*p*-NO$_2$C$_6$H$_4$, H$_o$), 8.125 (2 H, d, N-6-*p*-NO$_2$C$_6$H$_4$, H$_m$) 8.31 (4 H, br s, N-2-*p*-NO$_2$C$_6$H$_4$, H$_o$, H$_m$); δ_C(CDCl$_3$) 20.78 (Me), 23.95, 24.39, 30.34, 33.12 and 35.40 [(CH$_2$)$_5$], 85.77 (C-5), 94.31, 112.34 (C-6a and C-3a, respectively; bridgeheads), 140.43, 123.98, 124.42 and 147.65 (C-1′, C-2′, C-3′ and C-4′, respectively, N-2-*p*-NO$_2$C$_6$H$_4$) and 149.67, 117.2, 125.18 and 140.43 (C-1′, C-2′, C-3′ and C-4′, respectively, N-6-*p*-NO$_2$C$_6$H$_4$).

(v) 4-(p-*Nitrophenyl*)-2,6-*diphenyl*-4H-1,3,4,5-*oxatriazine* **9C**.—A solution of compound **4Cf** (0.25 g, 0.492 mmol) in ethanol (10 cm^3) was treated with acetic acid (5 cm^3) and the mixture was heated under reflux for 20 min. On cooling of the mixture compound **9C** separated as a yellow solid (0.15 g, 85%), m.p. 224–225 °C (EtOH); ν_{max}(Nujol)/cm^{-1} 1591 (C=N); δ_H(CDCl$_3$) 7.47–7.56 (6 H, m, ArH), 7.62 (2 H, d, J_{AB} 9.5, N-4-*p*-NO$_2$C$_6$H$_4$, H$_m$), 8.015 (4 H, m, ArH), 8.215 (2 H, d, N-4-*p*-NO$_2$C$_6$H$_4$, H$_o$); δ_C(CDCl$_3$) 146.4 (C=N), 128.0, 126.5, 128.85 and 131.95 (C-1′, C-2′, C-3′ and C-4′, respectively, C-2 and C-6-phenyl) and 150.0, 113.7, 125.2 and 142.1 (C-1′, C-2′, C-3′, C-4′, respectively, N-4-*p*-NO$_2$C$_6$H$_4$).

(vi) 2-*Phenyl*-1,2,3-*triazaspiro*[4.4]*non*-1-*en*-2-*ylium*-3-*id*-4-*one* **10A**.—A solution of compound **5Af** (0.5 g, 1.56 mmol) in ethanol (10 cm^3) was treated with acetic acid (5 cm^3) and the mixture was heated under reflux for 30 min. Evaporation of the solvent under reduced pressure gave an oily residue which was purified by column chromatography using Merck silica gel (230–400 mesh ASTM) eluting with chloroform to give compound **10A** as a light brown oil, which solidified to a waxy solid with time (0.3 g, 89%), m.p. 73–75 °C; ν_{max}/cm^{-1} 1701 (C=O), 1529 [N=N$^+$(Ar)N$^-$]; δ_H(CDCl$_3$) 2.12–2.16 [8 H, m, (CH$_2$)$_4$], 7.55–7.70 (3 H, m, ArH), 8.33–8.37 (2 H, m, N-2-phenyl, H$_o$); δ_C(CDCl$_3$) 26.9, 37.75 [(CH$_2$)$_4$], 85.1 (C-5; spiro-C), 140.0, 122.4, 129.35 and 133.4 (C-1′, C-2′, C-3′ and C-4′, respectively; N-2-phenyl) and 196.0 (C=O).

Kinetic Measurements.—A specific quantity (*ca.* 30 mg, 0.0607 mmol) of the oxazolo[4,5-*d*]-1,2,3-triazole **4** was dissolved in CDCl$_3$ (1 cm^3) and the solution was filtered into a NMR tube. The tube was then placed in the probe of a JEOL-JNM-GX 270 FT NMR spectrometer and equilibrated at 50 °C. Once the solution reached the required constant temperature (monitored using a thermocouple and a methanol standard sample), the tube was briefly removed and deuteriated acetic acid (1.33 mmol) was added to it. Once the sample was re-equilibrated at a constant temperature of 50 °C, the spectrum was recorded. The subsequent spectra were recorded at specific time intervals until the reaction was completed (I = 0).

The rates of disappearance of oxazolo[4,5-*d*]-1,2,3-triazoles were obtained from plots of $\log(I_t - I_\infty)$ for the 5-H$_A$ methine signal (I = intensity) *vs.* time. These plots were linear with slopes of $-k/2.303$ where k is the rate constant for substrate consumption. The rates of appearance of the oxatriazine products were similarly obtained from linear plots of $\log(I_\infty - I_t)$ for the growing oxatriazine phenyl peak at 8.02 ppm *vs.* time, with slope of $-k/2.303$ (where k is the rate constant for product appearance), but the infinity values for these were less reliable. A typical run is shown in Fig. 1.

Acknowledgements

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