Fused *v*-Triazolo-heterocycles. Synthesis of 4*H*-*v*-Triazolo[1,5-*d*][1,3,4]oxadiazines[1]

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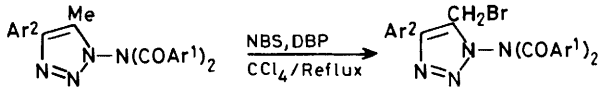
The synthesis of some 4*H*-*v*-triazolo[1,5-*d*][1,3,4]oxadiazine derivatives, which constitute a novel heterocyclic ring system, is described. They are prepared by heating of the corresponding 5-bromomethyl-1-(*N*,*N*-diaroylamino)-*v*-triazoles. The spectroscopic data of these new compounds are also reported.

Following our previous studies on *v*-triazole derivatives[2–4] we have now prepared several 4-aryl-5-bromomethyl-1-(*N*,*N*-diaroylamino)-*v*-triazoles (**2**) from the corresponding 5-methyl-derivatives (**1**), in order to use them as starting materials in the synthesis of fused *v*-triazolo-heterocycles.

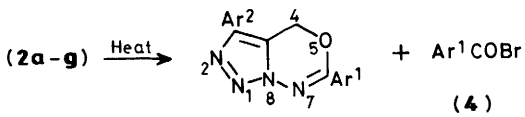


(**1**) (**2**)

a; $Ar^2 = Ar^1 = Ph$
b; $Ar^2 = Ph$, $Ar^1 = p\text{-}MeOC_6H_4$
c; $Ar^2 = Ph$, $Ar^1 = p\text{-}ClC_6H_4$
d; $Ar^2 = Ph$, $Ar^1 = o\text{-}ClC_6H_4$
e; $Ar^2 = Ph$, $Ar^1 = o\text{-}O_2NC_6H_4$
f; $Ar^2 = p\text{-}MeOC_6H_4$, $Ar^1 = Ph$
g; $Ar^2 = p\text{-}ClC_6H_4$, $Ar^1 = Ph$

Compounds (**2**) were prepared in good yield by reaction of (**1**) with *N*-bromosuccinimide (NBS) in carbon tetrachloride in the presence of dibenzoyl peroxide (DBP). They are stable crystalline compounds. Their i.r. spectra show peaks for $\nu_{C=O}$ at 1 720—1 750 cm^{-1}. In the ^1H n.m.r. spectra, the CH_2Br protons appeared at δ 4.6—4.8 and in their mass spectrum they showed the molecular ion peak ($M^{+\bullet}$), as well as peaks corresponding to the ions $M - 28^+$, Ar^1CO^+, $Ar^2\text{–}C{\equiv}C\text{–}CH_2Br^{+\bullet}$, and $Ar^2\text{–}C{\equiv}C\text{-}CH_2^+$. Their analytical and spectral data are given in the Table.

We have found that heating of the compounds (**2**) at temperatures above their melting points (170—200 °C) leads to the formation of the 4*H*-3,6-diaryl-*v*-triazolo[1,5-*d*][1,3,4]-oxadiazines (**3**) and the corresponding aroyl bromides (**4**). In the

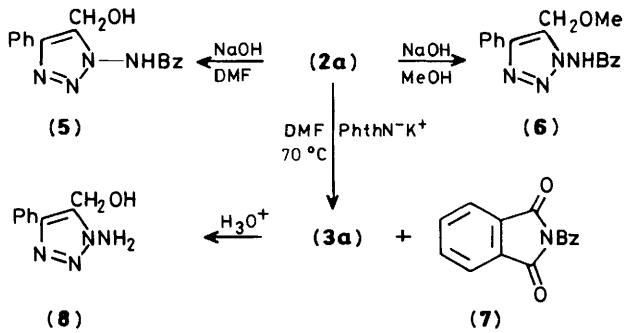


(**4**)

(**3a-g**)

case of the compounds (**2**) with melting points higher than 200 °C, as well as for the derivatives with an *ortho*-substituent in the aroyl moiety (**2d**, **e**), the yields of the *v*-triazolo-oxadiazines (**3**) were very poor, because of decomposition of the reaction products. Better results were obtained when the reaction was carried out in a tetralin solution in the presence of potassium or sodium carbonate and at lower temperatures, *i.e.* between 150 and 170 °C. The above method is analogous to that of van Alphen,[5] who first synthesized the 4,5-dihydro-6*H*-1,3,4-oxadiazine ring system by heating *N'*-chloroacetylhydrazides and related compounds with sodium carbonate in acetone in a sealed tube. Other reported preparations of this heterocyclic ring are based on the cyclization of the appropriate derivatives of acylhydrazides.[6–9]

Reaction of (**2a**) with sodium hydroxide in dimethylformamide (DMF), by a method analogous to that reported by Gaozza and Laudan,[7] failed to give the expected (**3a**), but gave instead the 1-benzamido-5-hydroxymethyl-*v*-triazole (**5**). Treatment of (**2a**) with sodium hydroxide in a methanolic solution gave the 5-methoxymethyl-derivative (**6**). Treatment of (**2a**) with potassium phthalimide ($PhthN^-K^+$) in DMF gave compound (**3a**) and *N*-benzoylphthalimide (**7**).



The structures of compounds (**3**) have been established by examining their analytical and spectral data. Thus, in the i.r. spectrum they showed a weak peak at 1 620 cm^{-1}, which is attributed to the C=N bond stretching vibration. In the ^1H n.m.r. spectrum, taken in $CDCl_3$ the methylenic protons of the oxadiazine ring resonated at δ 5.8—5.9, whereas the aromatic protons gave the expected pattern for the two aryl rings. The CH_2O carbon appeared in the ^{13}C n.m.r. spectrum at *ca.* 63 p.p.m., whereas a peak at *ca.* 154 p.p.m. was in accord with the presence of the C=N carbon[10] of the oxadiazine ring. In the mass spectrum, besides the molecular ion peak ($M^{+\bullet}$), they gave also peaks corresponding to the $M - 28^{+\bullet}$ ion (which is characteristic for the triazole ring)[11] and also peaks corresponding to the Ar^1CO^+ and $Ar^1CN^{+\bullet}$ ions as well as to the $Ar^2\text{–}C{\equiv}C\text{–}CH_2O^+$ and $Ar^2\text{–}C{\equiv}C\text{–}CH_2^+$ fragments.

Heating of compound (**3a**) with concentrated hydrochloric acid gave the 1-amino-4-phenyl-*v*-triazole (**8**), which is in agreement[7] with structure (**3**).

Experimental

M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected. I.r. spectra were recorded as Nujol mulls on

Table. Physical, spectral, and analytical data for compounds (**2**)

No.	M.p. (°C)	Yield (%)	Solvent*	$\nu_{max.}$/cm^{-1} (nujol) (C=O)	^{1}H n.m.r. (δ, $CDCl_3$) CH_2Br	Aroyl groups (Ar^1CO) *o*-	Aroyl groups (Ar^1CO) *m*-,*p*-	4-Aryl group (Ar^2) *o*-	4-Aryl group (Ar^2) *m*-,*p*-	Mass spectrum *m*/*z* (r.i.)	Formula	Found (Required %) C	H	N
(2a)	142—144	70	Benzene–LP	1 735 1 710	4.60 (2 H, s)	7.90 (4 H, m)	*ca.* 7.5 (11 H, m)	*ca.* 7.5 (11 H, m)	*ca.* 7.5 (11 H, m)	462, 460 (M^+) 434, 432 ($M^+ - 28$) 196, 194, 115, 105 (100)	$C_{23}H_{17}BrN_4O_2$	60.15 (59.88)	3.8 (3.71)	12.15 (12.14)
(2b)	132—134	85	Benzene–LP	1 715 1 700	4.60 (2 H, s)	7.94 (4 H, d)	6.88 (4 H, d)	7.82 (2 H, m)	7.46 (3 H, m)	494, 492 ($M^+ - 28$) 196,194, 135 (100), 115	$C_{25}H_{21}BrN_4O_4$	57.4 (57.59)	4.0 (4.06)	10.55 (10.75)
(2c)	205—207	85	Benzene–LP	1 740 1 720	4.56 2 H, s)	7.89 (4 H, d)	7.43 (7 H, m)	7.79 (2 H, m)	7.43 (7 H, m)	530, 528 (M^+) 502, 500 ($M^+ - 28$) 196, 194, 139 (100), 115	$C_{23}H_{15}BrCl_2N_4O_2$	52.35 (52.11)	2.7 (2.85)	10.5 (10.57)
(2d)	206—209	90	CH_2Cl_2–Et_2O	1 740 1 730 1 712	4.68 (2 H, s)	7.78 (4 H, m)	7.29 (6 H, m)	7.78 (4 H, m)	7.49 (3 H, m)	530, 528 (M^+) 502, 500 ($M^+ - 28$) 196, 194, 139 (100), 115	$C_{23}H_{15}BrCl_2N_4O_2$	52.25 (52.11)	2.75 (2.85)	10.7 (10.57)
(2e)	207—210	90	CH_2Cl_2–Et_2O	1 750 1 740	4.80 (2 H, s)	*ca.* 7.7 (8 H, m)	8.27 (2 H, m)	*ca.* 7.7 (8 H, m)	7.46 (3 H, m)		$C_{23}H_{15}BrN_6O_6$	50.05 (50.11)	2.75 (2.74)	14.95 (15.24)
(2f)	146—148	80	Benzene–LP	1 735 1 710	4.59 (2 H, s)	7.93 (4 H, m)	7.41 (6 H, m)	7.75 (2 H, d)	7.02 (2 H, d)	492, 490 (M^+) 464, 462 ($M^+ - 28$) 145, 105 (100)	$C_{24}H_{19}BrN_4O_3$	58.45 (58.67)	3.85 (3.90)	11.25 (11.40)
(2g)	173—176	75	CH_2Cl_2–Et_2O	1 745 1 715	4.58 (2 H, s)	7.92 (4 H, m)	7.45 (8 H, m)	7.75 (2 H, d)	7.45 (8 H, m)	496, 494 (M^+) 468, 466 ($M^+ - 28$) 149,105 (100)	$C_{23}H_{16}BrClN_4O_2$	55.75 (55.72)	3.25 (3.25)	11.45 (11.30)

* LP = Light petroleum.

a Perkin-Elmer 257 spectrometer. ^{1}H N.m.r. and ^{13}C n.m.r. spectra were obtained on a Varian CFT-20 spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as internal standard. The mass spectra were obtained on a Hitachi–Perkin-Elmer RMU 6L spectrometer and elemental microanalyses were performed with a Perkin-Elmer 240 analyser. Column chromatography was performed over Merck Kieselgel 60, particle size 0.063—0.200 mm. Light petroleum refers to that fraction of b.p. 60—80 °C. Ether refers to diethyl ether.

Compounds (**1**).—These were prepared by thermal isomerization from the corresponding triazolyl-isoimides as previously described,[12,13] and their analytical and spectral data were in agreement with their structure.[4,13]

4-*Aryl*-5-*bromomethyl*-1-(N,N-*diaroylamino*)-v-*triazoles* (**2**). *General Procedure.*—To a refluxing solution of (**1**) (5 mmol) in carbon tetrachloride (50 ml) were added recrystallized *N*-bromosuccinimide (1.0 g, 5.5 mmol) and dibenzoyl peroxide (0.3 g). The mixture was refluxed for a further 4—6 h and the succinimide formed was filtered off. The filtrate was washed with water (4 × 20 ml), dried and evaporated. The 5-bromomethyl derivative (**2**) crystallized on treatment with ether, and was isolated by filtration. This product was pure enough for further reaction. For elemental analysis it was recrystallized from CH_2Cl_2–ether or C_6H_6–light petroleum. Analytical and spectral data of compounds (**2**) are given in the Table.

4H-3,6-*Diaryl*-v-*triazolo*[1,5-d][1,3,4]*oxadiazines* (**3**): *General Procedure.*—*Method A.* Compound (**2**) (0.1—1.0 mmol) was heated in an oil-bath at 180—190 °C for 30 min. For compounds (**2**) which have higher m.p.s, the temperature was raised to their m.p.s; the solids, on melting, turned dark brown. After cooling, the solidified brown mass was washed on a glass filter with ether in order to remove aroyl bromide. The *v*-triazolo-oxadiazine (**3**) was isolated and recrystallized from dichloromethane–ether. Better purification was achieved by sublimation of the crude product at 180—190 °C at 0.2—0.5 mmHg, or by column chromatography over SiO_2 using ethyl acetate–light petroleum (2:8) as eluant. The aroyl bromide (**4**) was then either isolated from the ether washings and identified by its i.r. spectrum, or it was hydrolysed and isolated as the corresponding substituted benzoic acid.

Method B. A mixture of (**2**) (0.5—1.0 mmol) and anhydrous potassium carbonate (0.2 g, 1.5 mmol), (or the equivalent amount of anhydrous sodium carbonate), in tetralin (4 ml) dried over 4 Å molecular sieves, was heated at 160—170 °C for 40 min. After cooling, CH_2Cl_2 (30 ml) was added and the mixture was washed with water (2 × 20 ml). The solution was then dried and the CH_2Cl_2 removed. With time, crystals of the *v*-triazolo-oxadiazine (**3**) precipitated from the tetralin solution and these were filtered off, washed with ether, and recrystallized from the appropriate solvents.

4H-3,6-*Diphenyl*-v-*triazolo*[1,5-d][1,3,4]*oxadiazine* (**3a**).—*Method A.* Compound (**2a**) (0.7 g, 1.5 mmol) was heated at 190 °C for 30 min to give the *v*-triazolo-oxadiazine (**3a**) (0.22 g, 53%), m.p. 237 °C (subl.) (Found: C, 70.0; H, 4.4; N, 20.25. $C_{16}H_{12}N_4O$ requires C, 69.55; H, 4.38; N, 20.28%); $\nu_{max.}$ 1 620 (C=N) cm^{-1}; δ_H 5.80 (2 H, s, CH_2O), 7.53 (8 H, m), and 8.12 (2 H, m); δ_C (20 MHz, $CDCl_3$) 63.4 (CH_2O), and 154.4 (C=N); *m/z* 276 (M^+, 1.5%), 248 (M^+ − 28, 1.3%), 115 (49%), and 105 (Ar^1CO^+, 100%).

4H-6-p-*Methoxyphenyl*-3-*phenyl*-v-*triazolo*[1,5-d][1,3,4]-*oxadiazine* (**3b**).—*Method A.* Compound (**2b**) (0.52 g, 1 mmol) was heated at 180 °C for 30 min to give the *v*-triazolo-oxadiazine (**3b**) (0.2 g, 66%), m.p. 230—232 °C (from CH_2Cl_2–ether) (Found: C, 67.0; H, 4.55; N, 17.95. $C_{17}H_{14}N_4O_2$ requires C, 66.66; H, 4.61; N, 18.29%); $\nu_{max.}$ 1 610 (C=N) cm^{-1}; δ_H 5.82 (2 H, s, CH_2O), 3.86 (3 H, s, MeO), 6.93 (2 H, d), 7.40 (3 H, m), 7.58 (2 H, m), and 8.18 (2 H, d); δ_C (20 MHz, $CDCl_3$) 63.2 (CH_2O), 153.8 (C=N); *m/z* 306 (M^+, 1.6%), 278 (M^+ − 28, 2.5%), 135 (Ar^1CO^+, 100%), and 115 (24%).

4H-6-p-*Chlorophenyl*-3-*phenyl*-v-*triazolo*[1,5-d][1,3,4]-*oxadiazine* (**3c**).—*Method B.* A mixture of (**2c**) (0.22 g, 0.41 mmol) and K_2CO_3 (0.1 g, 0.7 mmol) in tetralin (3 ml) was heated at 180 °C for 50 min to give the *v*-triazolo-oxadiazine (**3c**) (0.03 g, 24%), m.p. 260—262 °C (Found: C, 62.05; H, 3.25; N, 18.1. $C_{16}H_{11}ClN_4O$ requires C, 61.85; H, 3.57; N, 18.03%); $\nu_{max.}$ 1 610 (C=N) cm^{-1}; δ_H 5.90 (2 H, s, CH_2O), 7.45 (5 H, m), 7.61 (2 H, m), and 8.05 (2 H, d); *m/z* 310 (M^+, 1.1%), 282 (M^+ − 28, 2.2%), 139 (Ar^1CO^+, 100%), and 115 (76%).

Method A. Compound (**2c**) (0.2 g, 0.38 mmol) was heated at 205 °C for 40 min to give a crude product, m.p. 200—250 °C. This was chromatographed on SiO_2 (using $CHCl_3$ as eluant) to give the *v*-triazolo-oxadiazine (**3c**) (0.013 g, 11%), m.p. 252—256 °C, which was identical with that isolated by method B.

4H-6-o-*Chlorophenyl*-3-*phenyl*-v-*triazolo*[1,5-d][1,3,4]-*oxadiazine* (**3d**).—*Method B.* A mixture of (**2d**) (0.8 g, 1.5 mmol) and Na_2CO_3 (0.2, 2 mmol) in tetralin (4 ml) was heated at 170 °C for 40 min to give a crude product (0.17 g) which was chromatographed on SiO_2 using ethyl acetate–light petroleum (2:8) as eluant to give the *v*-triazolo-oxadiazine (**3d**) (0.093 g, 20%), m.p. 172—174 °C (from CH_2Cl_2–ether–light petroleum) (Found: C, 61.75; H, 3.55; N, 17.95. $C_{16}H_{11}ClN_4O$ requires C, 61.85; H, 3.57; N, 18.03%); $\nu_{max.}$ 1 620 (C=N) cm^{-1}; δ_H 5.90 (2 H, s, CH_2O), 7.44 (5 H, m), 7.62 (2 H, m), *ca.* 7.8 (1 H, m); *m/z* 310 (M^+, 1%), 282 (M^+ − 28, 1%), 139 (Ar^1CO^+, 100%), and 115 (80%).

4H-6-o-*Nitrophenyl*-3-*phenyl*-v-*triazolo*[1,5-d][1,3,4]-*oxadiazine* (**3e**).—*Method B.* A mixture of (**2e**) (0.276 g, 0.5 mmol) and K_2CO_3 (0.15 g, 1 mmol) in tetralin (4 ml) was heated at 170 °C for 50 min to give the *v*-triazolo-oxadiazine (**3e**) (0.03 g, 19%), m.p. 228—230 °C (from CH_2Cl_2–ether) (Found: C, 59.7; H, 3.35; N, 21.65. $C_{16}H_{11}N_5O_3$ requires C, 59.81; H, 3.45; N, 21.8); $\nu_{max.}$ 1 620 (C=N) cm^{-1}; δ_H 5.82 (2 H, s, CH_2O), 7.45 (3 H, m), *ca.* 7.7 (4 H, m), and 8.05 (2 H, m); *m/z* 321 (M^+, 0.3%), 293 (M^+ − 28, 0.6%), 150 (Ar^1CO^+, 18%), and 115 (100%).

4H-3-p-*Methoxyphenyl*-6-*phenyl*-v-*triazolo*[1,5-d][1,3,4]-*oxadiazine* (**3f**).—*Method A.* Compound (**2f**) (0.66 g, 1.3 mmol) was heated at 170 °C for 30 min to give the *v*-triazolo-oxadiazine (**3f**) (0.16 g, 39%), m.p. 223—225 °C (subl.) (Found: C, 66.35; H, 4.55; N, 18.4. $C_{17}H_{14}N_4O_2$ requires C, 66.66; H, 4.61; N, 18.29%); $\nu_{max.}$ 1 615 (C=N) cm^{-1}; δ_H 3.82 (3 H, s, MeO), 5.82 (2 H, s, CH_2O), 6.94 (2 H, d), 7.50 (5 H, m), and 8.06 (2 H, m); δ_C (20 MHz, $CDCl_3$) 63.3 (CH_2O), and 154.4 (C=N); *m/z* 306 (M^+, 2.8%), 278 (M^+ − 28, 1%), 145 (100%), and 105 (Ar^1CO^+, 74%).

4H-3-p-*Chlorophenyl*-6-*phenyl*-v-*triazolo*[1,5-d][1,3,4]-*oxadiazine* (**3g**).—*Method B.* A mixture of (**2g**) (0.496 g, 1 mmol) and K_2CO_3 (0.2 g, 1.5 mmol) in tetralin (4 ml) was heated at 170 °C for 50 min to give the *v*-triazolo-oxadiazine (**3g**) (0.1 g, 33%), m.p. 289—291 °C (from $CHCl_3$) (Found: C, 61.5; H, 3.5; N, 17.95. $C_{16}H_{11}ClN_4O$ requires C, 61.85; H, 3.57; N, 18.03%); $\nu_{max.}$ 1 620 (C=N) cm^{-1}; δ_H 5.86 (2 H, s, CH_2O), 7.40 (2 H, d), *ca.* 7.5 (5 H, m), and 8.07 (2 H, m); *m/z* 310 (M^+, 1.5%), 282 (M^+ − 28, 0.3%), 149 (20%), 105 (Ar^1CO^+, 100%).

Reaction of (**2a**) *with Potassium Phthalimide in* DMF.—A mixture of (**2a**) (0.23 g, 0.5 mmol) and potassium phthalimide (0.13 g, 0.7 mmol) in DMF (5 ml) was stirred at 25 °C for 40 min

and then heated at 70 °C for 20 min. The mixture was cooled, diluted with water (70 ml) and extracted with $CHCl_3$ (30 ml). The chloroform solution was washed with 0.2M-NaOH (20 ml) and water (20 ml), and upon evaporation gave an oily mass; this, on treatment with ethyl ether, gave white crystals (0.027 g, 20%), m.p. 235—237 °C, of the *v*-triazolo-oxadiazine (**3a**) identical with an authentic specimen by i.r., ^1H n.m.r., and mass spectroscopy. From the ether solution a crystalline product (0.025 g) was precipitated, which was identified as the *N*-benzoylphthalimide (**7**), m.p. 158—163 °C (lit.,[14] 169 °C); $\nu_{max.}$ 1 790, 1 760, 1 740, and 1 700 cm^{-1}; *m/z* 251 (M^+, 88%), 223 ($M^+ - 28$, 28%), and 105 ($PhCO^+$, 100%).

Acid Hydrolysis of (**3a**).—A solution of *v*-triazolo-oxadiazine (**3a**) (0.14 g, 0.5 mmol) in concentrated hydrochloric acid (7 ml) was refluxed for 2 h, after which it was made alkaline (Na_2CO_3, pH 8) and extracted with CH_2Cl_2 (60 ml). Evaporation of the solvent from the extract gave the 5-hydroxymethyl-4-phenyl-1-amino-*v*-triazole (**8**) (0.034 g, 37%), m.p. 161—163 °C (from MeOH–Et_2O) (Found: C, 56.75; H, 5.3; N, 29.3. $C_9H_{10}N_4O$ requires C, 56.83; H, 5.30; N, 29.45%); $\nu_{max.}$ 3 370, 3 340, 3 200br, and 1 610 cm^{-1}; δ_H {$CDCl_3$ + [$(CD_3)_2SO$]} 4.77 (2 H, s, CH_2O), 6.20 (1 H, s, exchangeable with D_2O, OH), 7.40 (3 H, m), and 7.80 (2 H, m); *m/z* 191 ($M^+ + 1$, 2%), 190 (M^+, 1.6%), 189 ($M^+ - 1$, 2.3%), 175 ($M^+ - 15$, 1.4%), 173 ($M^+ - 17$, 1.4%), 162 ($M^+ - 28$, 11%), 149 (64%), 131 ($PhC{\equiv}CCH_2OH^+$, 100%), and 115 (93%).

Reaction of (**2a**) *with* NaOH *in* MeOH.—To a mixture of NaOH (1.0 g) in MeOH (10 ml) a solution of (**2a**) (0.115 g, 0.25 mmol) in MeOH (5 ml) was added and the mixture was heated at 60 °C for 3 h; it was then diluted with water (70 ml) and extracted with $CHCl_3$ (30 ml). The alkaline solution was acidified (pH 2) and extracted with $CHCl_3$ (50 ml). The extract was evaporated to give an oily mass which, on treatment with ether–light petroleum, gave the 1-benzamido-5-methoxymethyl-4-phenyl-*v*-triazole (**6**) (0.055 g, 71%), m.p. 128—131 °C (from ether–light petroleum) (Found: C, 66.1; H, 5.2; N, 18.45. $C_{17}H_{16}N_4O_2$ requires C, 66.22; H, 5.22; N, 18.17%); $\nu_{max.}$ 3 200 (NH), and 1 705 (C=O) cm^{-1}; δ_H 3.26 (3 H, s, MeO), 4.49 (2 H, s, CH_2O), 7.40 (6 H, m), 7.66 (2 H, m), 7.93 (2 H, m), and 11.0 (1 H, s, NH); *m/z* 308 (M^+, 0.4%), 280 ($M^+ - 28$, 6%), 146 ($PhC{\equiv}CCH_2OMe^+$, 8%), 115 (46%), and 105 (100%).

Reaction of (**2a**) *with* NaOH *in* DMF.—A mixture of (**2a**) (0.3 g, 0.65 mmol) and NaOH (0.2 g, 5 mmol) in DMF (5 ml) was heated at 100 °C for 2 h. The DMF was then removed on an evaporator and the residue washed repeatedly with CH_2Cl_2 and ether, after which the remaining solid was dissolved in water (20 ml) and acidified (pH 2), to precipitate 1-benzamido-5-hydroxymethyl-4-phenyl-*v*-triazole (**5**); this was filtered off (0.125 g, 65%), m.p. 214—216 °C (from MeOH) (Found: C, 65.1; H, 4.75; N, 19.35. $C_{16}H_{14}N_4O_2$ requires C, 65.30; H, 4.79; N, 19.04%); $\nu_{max.}$ 3 210br, 1 715, and 1 710 (C=O) cm^{-1}; δ_H {$CDCl_3$ + [$(CD_3)_2SO$]} 4.20 (1 H, br, exchangeable with D_2O, OH), 4.65 (2 H, s, CH_2O), 7.50 (6 H, m), 7.98 (4 H, m), and 12.2 (1 H, s, exchangeable with D_2O, NH); *m/z* 294 (M^+, 0.3%), 266 ($M^+ - 28$, 3.7%), 132 ($PhC{\equiv}CCH_2OH^+$, 19%), 131 ($PhC{\equiv}CCH_2O^+$, 22%), 115 (25%), 105 (98%), and 103 (100%).

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