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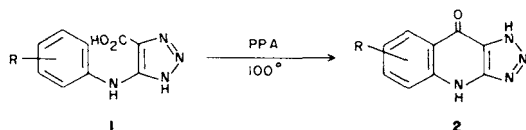
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Ethyl 1-benzyl-5-chloro-*v*-triazole-4-carboxylate (**3**) undergoes facile nucleophilic displacement of the halogen atom with phenoxide ion to yield aryloxytriazolecarboxylates **4** which debenzylate under hydrogenolytic conditions to *N*-*H* triazoles **7**. Saponification and cyclization with either polyphosphoric acid or phosphoric oxide in methanesulphonic acid leads to the novel 9-oxo-1*H*,9*H*-benzopyrano[2,3-*d*]-*v*-triazole system **9**, members of which have potential as antiasthmatic agents.

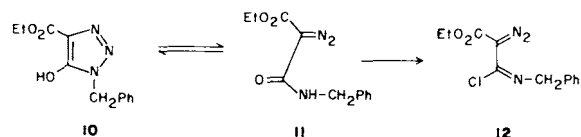
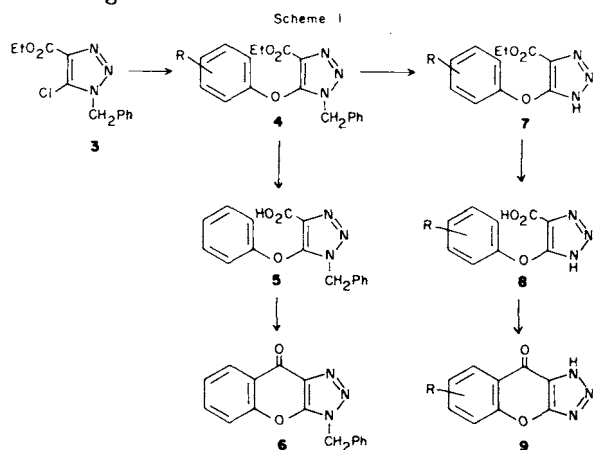
J. Heterocyclic Chem., **18**, 1117 (1981).

Recently, we reported the synthesis of several triazolo[4,5-*b*]quinolines **2** as part of a programme designed to produce antiallergic drugs (1). These compounds were prepared by cyclization of the corresponding anilino-triazolecarboxylic acids **1** with polyphosphoric acid (PPA).



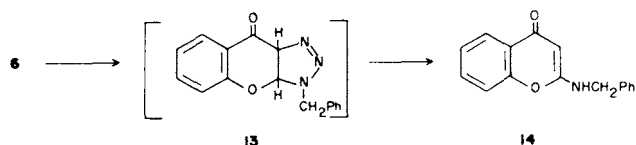
As a continuation of these studies we have prepared a series of oxa analogues of **2**, the benzopyrano[2,3-*d*]triazoles **9**, a novel class of heterocycles for which the route illustrated in Scheme I was used (2).

The precursor chlorotriazole **3** was synthesised from ethyl 1-benzyl-5-hydroxy-*v*-triazole-4-carboxylate (**10**) by a modification of the procedure of Hoover and Day (3) which we found to give unreproducible yields. Simple replacement of the solvent phosphorus oxychloride by toluene resulted in a marked improvement in the reaction and gave yields consistently in the order of 60-65% even in large scale preparations. A competing reaction, in which the hydroxytriazole **10** apparently underwent a Dimroth rearrangement to the diazoamide **11** with subsequent chlorination to the diazoimine **12**, was substantially reduced using these conditions.



Compound **3** underwent facile nucleophilic displacement of the halogen with phenoxide ion, generated *in situ*, in *N,N*-dimethylformamide to give good yields of the aryloxytriazolecarboxylates **4** (Table 1), and this constitutes a good method for the synthesis of compounds of this type. Saponification of the parent ester **4a** led quantitatively to the acid **5** which could be cyclized to the *N*-benzylbenzopyrano[2,3-*d*]triazole **6** by one of several routes. Indirect cyclization of **6** *via* a Friedel-Crafts reaction on its acid chloride was preferred over direct cyclization with either polyphosphoric acid or phosphoric oxide in methanesulphonic acid, the yields being higher and more reproducible under the indirect conditions.

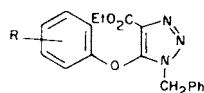
Although removal of *N*-benzyl groups from vicinal triazoles is known to be difficult (4) we were surprised at the stability of **6** to hydrogenolytic conditions. Even at 100° and 1000 psi over palladinized charcoal (5) compound **6** remained intact. Increasing the temperature a further 20°, however, resulted in a smooth reaction over 7 hours to a new product identified from analytical and spectral data as the benzylaminochromone **14**.



This compound, isolated in 95% yield, presumably arises from hydrogen addition across the bridgehead double bond to give the triazoline **13** followed by elimination of nitrogen.

Other reductive methods such as sodium in liquid ammonia, sodium naphthalene and potassium in tetrahydrofuran led only to extensive degradation. A low yield (ca. 12%) of debenzylated material **9a** was isolated using lithium in ethylamine but this is not a practical procedure.

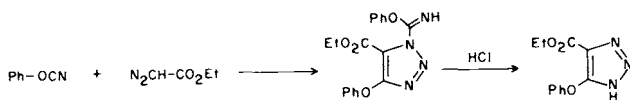
Table I

Ethyl 1-Benzyl-5-aryloxy-*v*-triazole-4-carboxylates

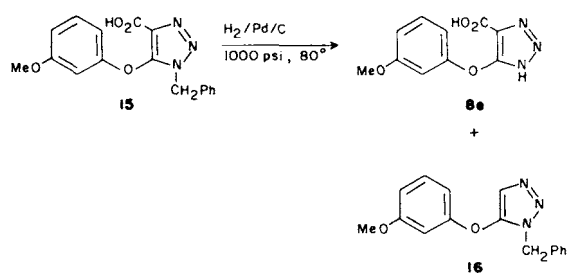
Compound No.	R	Mp °C	Recrystallization Solvent	Yield %	Formula	Analyses %		
						C	Calcd./Found H	N
4a	H	88-89	EtOH	78	C ₁₈ H ₁₇ N ₃ O ₃	66.85 66.7	5.3 5.45	13.0 13.1
4b	4 - Me	78	EtOH-H ₂ O	76	C ₁₉ H ₁₉ N ₃ O ₃	67.65 68.0	5.7 6.0	12.45 12.45
4c	4 - OMe	78-79	EtOH	71	C ₁₉ H ₁₉ N ₃ O ₄	64.6 64.75	5.4 5.35	11.9 11.95
4d	3 - OMe	52-53	Et ₂ O-petrol (bp 40-60°)	53	C ₁₉ H ₁₉ N ₃ O ₄	64.6 64.5	5.4 5.25	11.9 12.05
4e	4 - F	80-81	EtOH	77	C ₁₈ H ₁₆ FN ₃ O ₃	63.55 63.3	4.7 4.8	12.3 12.1
4f	2,3 - Me ₂	75-76	EtOH-H ₂ O	69	C ₂₀ H ₂₁ N ₃ O ₃	68.35 68.4	6.0 6.15	11.95 11.9
4g	3,4 - Me ₂	65-66	EtOH-H ₂ O	75	C ₂₀ H ₂₁ N ₃ O ₃	68.35 68.3	6.0 6.15	11.95 11.85
4h	3,4 - tetramethylene	73-74	Et ₂ O-petrol (bp 40-60°)	56	C ₂₂ H ₂₃ N ₃ O ₃	70.0 70.05	6.15 6.25	11.15 11.1
4i	2,3,5 - Me ₃	75	EtOH-H ₂ O	55	C ₂₁ H ₂₃ N ₃ O ₃	69.0 68.95	6.35 6.55	11.5 11.4

Fortunately, catalytic hydrogenolysis of the *N*-benzyl intermediates **4** under fairly forcing conditions led to a smooth debenzylation to the triazole esters **7** (Table II) and this is a useful procedure for the synthesis of compounds of this type. The parent compound **7a** has been synthesised by dipolar addition of ethyl diazoacetate to phenyl cyanate (**6**) (Scheme II) but the yields from this reaction were low.

Scheme II



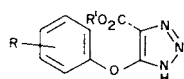
Alkaline hydrolysis of the triazole esters **7** leads to almost quantitative yields of the respective acids **8** (Table II). The methoxy compound **8e** was also prepared by hydrogenolysis of the acid **15** but the usefulness of this as a general method is limited by the ease of decarboxylation of triazole carboxylic acids under the reductive conditions and the aryloxytriazole **16** was a major by-product. In fact, thermolysis of **5** and its ring substituted derivatives is a good route to aryloxytriazoles of type **16**, the reaction usually being carried out at the melting point of the acid.



Cyclization of aryloxytriazolecarboxylic acids **8** to the tricyclic derivatives **9** can be carried out with either polyphosphoric acid or phosphoric oxide in methanesulphonic acid when reasonable yields of **9** are obtainable (Table III). Cyclization is possible *via* the acid chloride but in general interference from the free triazole *N*-H results in low yields of impure materials.

Asymmetric acids **8e**, **g** and **h** gave mixtures of the two possible isomers, as expected, but these were separated simply by a combination of fractional recrystallization and chromatography. It is of interest that both the 3,4-dimethylphenoxy **8g** and the 3,4-tetramethylenephenoxy **8h** derivatives yielded a greater abundance of the more hind-

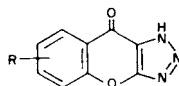
Table II

5-Aryloxy-1*H*-*v*-triazole-4-carboxylic Acids and Esters

Compound No.	R	R'	Mp °C	Recrystallization Solvent	Yield %	Formula	Analyses %		
							Calcd./Found	C	H N
7a	H	Et	96.5-98	MeOH-H ₂ O	88 (a)	C ₁₁ H ₁₁ N ₃ O ₃	Lit (6) mp 96-97°		
8a	H	H	141-142 dec	H ₂ O	90	C ₉ H ₇ N ₃ O ₃ ·O·5H ₂ O	50.45 50.3	3.75 3.75	19.6 19.45
7b	4 - Me	Et	94-97	EtOH-H ₂ O	97	C ₁₂ H ₁₃ N ₃ O ₃	58.3 58.35	5.3 5.4	17.0 17.0
8b	4 - Me	H	146-147 dec	EtOH-H ₂ O	86	C ₁₀ H ₉ N ₃ O ₃ ·0.5H ₂ O	52.65 52.85	4.4 4.2	18.4 18.55
7c	4 - OMe	Et	111-112	EtOH-H ₂ O	84	C ₁₂ H ₁₃ N ₃ O ₄	54.75 54.95	5.0 5.05	15.95 16.05
8c	4 - OMe	H	140 dec	H ₂ O	95	C ₁₀ H ₉ N ₃ O ₄ ·O·5H ₂ O	49.2 49.45	4.15 3.9	17.2 17.1
7d	3 - OMe	Et	104-105	EtOH-H ₂ O	71	C ₁₂ H ₁₃ N ₃ O ₄	54.75 54.9	5.0 4.9	15.95 15.7
8d	3 - OMe	H	137 dec	EtOAc-petrol	76	C ₁₀ H ₉ N ₃ O ₄	51.05 51.15	3.85 3.85	17.85 17.75
7e	4 - F	Et	123-124	toluene	96	C ₁₁ H ₁₀ FN ₃ O ₃	52.6 52.45	4.0 3.8	16.75 16.55
8e	4 - F	H	154 dec	EtOH-H ₂ O	93	C ₉ H ₆ FN ₃ O ₃ ·O·25H ₂ O	47.5 47.35	2.9 2.75	18.45 18.3
7f	2,3 - Me ₂	Et	99-100	EtOH-H ₂ O	76	C ₁₃ H ₁₅ N ₃ O ₃	59.75 59.95	5.8 5.6	16.1 15.95
8f	2,3 - Me ₂	H	132 dec	H ₂ O	76	C ₁₁ H ₁₁ N ₃ O ₃ ·H ₂ O	52.6 52.6	5.2 5.45	16.7 16.35
7g	3,4 - Me ₂	Et	65-66	toluene-petrol	64	C ₁₃ H ₁₅ N ₃ O ₃	59.75 59.9	5.8 5.8	16.1 16.15
8g	3,4 - Me ₂	H	144-145 dec	EtOH-H ₂ O	98	C ₁₁ H ₁₁ N ₃ O ₃	56.65 56.8	4.75 4.95	18.0 18.1
7h	3,4 - tetramethylene	Et	oil	— — —	83	C ₁₅ H ₁₇ N ₃ O ₃ (b)	62.7 62.65	5.95 6.2	14.65 14.05
8h	3,4 - tetramethylene	H	147 dec	Et ₂ O-petrol	83	C ₁₃ H ₁₃ N ₃ O ₃	60.2 60.4	5.05 5.15	16.2 15.85
7i	2,3,5 - Me ₃	Et	98	EtOH-H ₂ O	88	C ₁₄ H ₁₇ N ₃ O ₃ ·O·5H ₂ O	59.15 58.9	6.4 6.6	14.8 14.8
8i	2,3,5 - Me ₃	H	145 dec	EtOH-H ₂ O	60	C ₁₂ H ₁₃ N ₃ O ₃	58.3 58.55	5.3 5.7	17.0 16.6

(a) 26% yield by the procedure of D. Martin and A. Weise, *Chem. Ber.*, **99**, 317 (1966). (b) M⁺ 287.1270.

Table III
9-Oxo-1*H*,9*H*-benzopyrano[2,3-*d*]-*v*-triazoles



Compound No.	R	Mp °C dec (a)	Yield %	Cyclization Reagent	Formula	Analyses %		
						Calcd./Found	C	H N
9a	H	250-251	40	PPA	C ₉ H ₅ N ₃ O ₂		57.75 57.5	2.7 2.9 22.45 22.15
9b	7 - Me	252-255	69	PPA	C ₁₀ H ₇ N ₃ O ₂		59.7 59.5	3.5 3.7 20.9 20.65
9c	7 - OMe	263	32	P ₂ O ₅ /MSA	C ₁₀ H ₇ N ₃ O ₃		55.3 55.35	3.25 3.55 19.35 19.0
9d	6 - OMe	270-271	26	P ₂ O ₅ /MSA	C ₁₀ H ₇ N ₃ O ₃		55.3 54.95	3.25 3.55 19.35 19.5
9e	8 - OMe	258-260	12	P ₂ O ₅ /MSA	C ₁₀ H ₇ N ₃ O ₃		55.3 55.3	3.25 3.3 19.35 19.65
9f	5,6 - Me ₂	265-267	65	PPA	C ₁₁ H ₉ N ₃ O ₂		61.4 61.5	4.2 4.1 19.5 19.45
9g	6,7 - Me ₂	280-283	32	P ₂ O ₅ /MSA	C ₁₁ H ₉ N ₃ O ₂		61.4 61.05	4.2 3.9 19.5 19.35
9h	7,8 - Me ₂	251-252 (b)	64	P ₂ O ₅ /MSA	C ₁₁ H ₉ N ₃ O ₂		61.4 61.6	4.2 4.1 19.5 19.4
9i	6,7 - tetramethylene	244-246	26	PPA	C ₁₃ H ₁₁ N ₃ O ₂		64.7 65.0	4.6 4.55 17.4 17.6
9j	7,8 - tetramethylene	231-232	51	PPA	C ₁₃ H ₁₁ N ₃ O ₂		64.7 64.5	4.6 4.2 17.4 17.3
9k	5,6,8 - Me ₃	268-269	81	P ₂ O ₅ /MSA	C ₁₂ H ₁₁ N ₃ O ₂		62.85 62.85	4.85 5.1 18.35 18.4

(a) Recrystallised from ethanol. (b) Recrystallised from methanol.

ered isomers **9h** and **9j** respectively. The fluoro derivative **8e** cyclizes with difficulty under these conditions.

All derivatives of type **9** were inhibitors of rat passive cutaneous anaphylaxis whereas the *N*-benzyl compounds **6** were inactive. Detailed pharmacology will be reported elsewhere.

EXPERIMENTAL

Melting points were determined using a Büchi melting point apparatus and are uncorrected. Ir spectra were determined with a Perkin-Elmer 197 spectrophotometer as dispersions in nujol unless otherwise specified. Pmr spectra were obtained with a Varian EM 390 90 MHz spectrometer in the indicated solvents and were measured in ppm (δ) and J (Hz) with respect to TMS. Mass spectra were obtained on a VG-7770F spectrometer. Uv spectra were measured using a Perkin Elmer 554 spectrophotometer.

Ethyl 1-Benzyl-5-chloro-*v*-triazole-4-carboxylate (**3**).

A mixture of ethyl 1-benzyl-5-hydroxy-*v*-triazole-4-carboxylate (**3**) (46.00 g, 0.186 mole), phosphorus pentachloride (38.95 g, 0.187 mole) and dry toluene (500 ml) was heated to reflux for 90 minutes and the orange-red solution cooled. Removal of the solvent *in vacuo* afforded a red oil which was extracted with hot ether. The ethereal extracts were concentrated and petroleum ether (bp 40-60°) added to crystallize. Filtration at -80° gave 40 g of solid which recrystallized from petroleum ether (bp 60-80°) to give 32.17 g (65%) of **3** of mp 65.5-66.5° (lit (**3**) mp 67-68°).

Ethyl 5-Aryloxy-1-benzyl-*v*-triazole-4-carboxylates (**4**) (Table I).

General Procedure.

To a stirred solution of phenol (14.1 g, 0.15 mole) in dry *N,N*-dimethylformamide (200 ml) was added a 50% dispersion of sodium hydride in mineral oil (7.2 g, 0.15 mole) and the solution stirred for 1 hour at ambient temperature to ensure formation of the sodium salt. To this salt was added 39.9 g, 0.15 mole of **3** in a single portion and the mixture stirred at 70-80° for 24 hours. After cooling the solvent was removed

in vacuo and the residue partitioned between ethyl acetate and water. The organic phase was washed with dilute aqueous sodium hydroxide, brine and dried (magnesium sulfate). Evaporation of the solvent gave an oil which crystallised from ethanol after decolorization with charcoal to give 37.8 g (78%) of **4a** of mp 88-89°, ir: ν max 1707, 1563 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 1.00 (3H, t, $J = 7.5$ Hz, CH_3), 4.10 (2H, q, $J = 7.5$ Hz, CH_2CH_3), 5.37 (2H, s, CH_2Ph), 6.73 (2H, m), 7.20 (3H, m), 7.25 (5H, s, C_6H_5).

1-Benzyl-5-phenoxy-*v*-triazole-4-carboxylic Acid (**5**).

A mixture of **4a** (34.5 g, 0.107 mole) and 1.25*M* aqueous sodium hydroxide (186 ml) was stirred at 70° for 4 hours when solution was complete. The clear solution was cooled to 0° and cautiously acidified to give **5** as a white solid. Filtration and drying gave 31.4 g (100%) of material of mp 133-134° (from aqueous methanol); ir: ν max 2600 (broad), 1685, 1570 cm^{-1} ; $^1\text{H-nmr}$ ($\text{DMSO}-d_6$): δ 5.58 (2H, s, CH_2), 6.88 (2H, m), 7.21 (3H, m), 7.28 (5H, s, C_6H_5).

Anal. Calcd. for $\text{C}_{16}\text{H}_{13}\text{N}_3\text{O}_3$: C, 65.05; H, 4.45; N, 14.25. Found: C, 64.8; H, 4.45; N, 14.3.

3-Benzyl-9-oxo-9*H*-benzopyrano[2,3-*d'*]-*v*-triazole (**6**).

(a) Friedel-Crafts Cyclization.

To a solution of 14.8 g, 0.05 mole of **5** in thionyl chloride (160 ml) was added a catalytic amount of *N,N*-dimethylformamide and the mixture refluxed for 2 hours. After cooling the excess reagent was evaporated *in vacuo* and the residual acid chloride dissolved in dry dichloromethane (100 ml). Anhydrous aluminium chloride (20 g, 0.15 mole) was added over 30 minutes to the stirred solution at 0° and the mixture stirred for a further 3 hours at ambient temperature. After pouring onto ice-dilute hydrochloric acid the product was extracted into chloroform. The organic phase was washed with water then brine and dried (magnesium sulfate). Evaporation afforded a crystalline solid which on recrystallisation from ethanol-chloroform gave 9.02 g (63%) of **6** of mp 196° dec; ir: ν max 1688, 1610, 1565, 1535 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform) δ 5.62 (2H, s, CH_2), 7.32 (5H, s, C_6H_5), 7.45 (3H, m, CH-5,6,7), 8.33 (1H, dd, $J = 8$ Hz, 1.5 Hz, CH-8); uv (ethanol): λ max 219 (25,600), 263 (14, 100) 300 (6, 800) nm.

Anal. Calcd. for $\text{C}_{16}\text{H}_{11}\text{N}_3\text{O}_2$: C, 69.3; H, 4.0; N, 15.15. Found: C, 69.45; H, 3.75; N, 14.95.

(b) Phosphoric Oxide-Methanesulphonic Acid Cyclization.

Phosphoric oxide (8 g) was added with vigorous stirring to 98% methanesulphonic acid (20 ml) at 90° and when the solution was homogeneous 1.00 g, 0.0034 mole of **5** was added. The light brown solution was stirred at 95° for 24 hours, cooled and poured onto ice-water. The precipitated white solid was filtered, washed with water and dried. Chromatography on silica eluting with chloroform afforded 0.27 g (29%) of **6** identical with that produced in (a).

(c) Polyphosphoric Acid Cyclization.

Compound (**5**) (1.00 g, 0.0034 mole) was added to 85% polyphosphoric acid (11 g) at 96° and stirred at this temperature for 24 hours. Work-up as described for (b) above gave 0.11 g (12%) of compound **6** identical with that produced in (a).

Hydrogenolysis of (**6**).

A solution of **6** (1.4 g) in ethanol (300 ml) was hydrogenated over palladium on charcoal (0.3 g, of 10%) at 1100 psi and 120° for 7 hours. No **6** remained. The catalyst was removed from the cooled solution by filtration and the filtrate evaporated *in vacuo* to a yellow crystalline solid. Chromatography on silica gel eluting first with chloroform and then with 5% methanol-chloroform gave 1.1 g (95%) of 2-benzylaminochromone (**14**) of mp 165-168° (from ethanol); ir: ν max 3220, 1625 (sh), 1605, 1550, 1525 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 4.40 (2H, d, $J = 5.8$ Hz, collapses to a singlet on addition of deuterium oxide, CH_2), 6.02 (1H, distorted t, exchangeable, NH), 7.32 (8H, m, CH-6,7 and 8 and C_6H_5), 8.12 (1H, dd CH-5), M^+ 251 mu.

Anal. Calcd. for $\text{C}_{16}\text{H}_{13}\text{NO}_2$: C, 76.5; H, 5.2; N, 5.55. Found: C, 76.2; H, 5.3; N, 5.5.

Ethyl 5-Aryloxy-1*H*-*v*-triazole-4-carboxylates (**7**, Table II).

General Procedure.

A solution of ethyl 1-benzyl-5-phenoxy-*v*-triazole-4-carboxylate (**4a**, 22.0 g) in ethanol (300 ml) was hydrogenated at 100° and 1000 psi over 10% palladized charcoal (0.2 g) for 2-3 hours. No **4a** remained. The catalyst was removed from the cooled solution by filtration and the filtrate evaporated to an oil which crystallised from aqueous methanol to give 14.0 g (88%) of **7a** of mp 96.5-98° (lit (6) mp 96-97°); ir: ν max 3140, 1680, 1520 cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 1.28 (3H, t, $J = 7$ Hz, CH_3), 4.38 (2H, q, $J = 7$ Hz, CH_2), 7.01-7.50 (5H, m), 1 broad low field exchangeable proton.

5-Aryloxy-1*H*-*v*-triazole-4-carboxylic Acids (**8**, Table II).

General Procedure.

A solution of ethyl 5-phenoxy-1*H*-*v*-triazole-4-carboxylate (**7a**, 2.33 g, 1 mmole) in 1.25*M* aqueous sodium hydroxide (55 ml) was stirred at 70-80° for 2-3 hours and the solution was cooled to 0°. Cautious acidification with hydrochloric acid resulted in precipitation of the acid **8a** as a white crystalline solid. Filtration and recrystallisation from water furnished 1.84 g (90%) of **8a** of mp 141-142° dec; ir: ν max 3130, 2600, (broad), 1720, 1700, 1550 cm^{-1} .

9-Oxo-1*H*,9*H*-benzopyrano[2,3-*d'*]-*v*-triazoles (**9**, Table III).

General Procedures.

(a) Using Polyphosphoric Acid.

Finely powdered 5-phenoxy-1*H*-*v*-triazole-4-carboxylic acid (**8a**, 1.00 g) was added to 85% polyphosphoric acid (12 g) at 60° and the resulting solution was stirred at 100° for 24 hours. The cooled solution was diluted with ice-water and the product which separated was filtered off, washed with water and dried. Recrystallisation from ethanol afforded 0.36 g (40%) of **9a** of mp 250-251° dec; ir: ν max 2700 (broad), 1650, 1638, 1605, 1560 cm^{-1} ; $^1\text{H-nmr}$ ($\text{DMSO}-d_6$): δ 7.7 (3H, m, CH-5, 6 and 7), 8.28 (1H, dd, $J = 2$ Hz, 10 Hz, CH-8); uv (ethanol): λ max 220 (17,300), 268 (10,700), 316 (5,700) nm; m/s : M^+ 187.0382 ($\text{C}_9\text{H}_7\text{N}_3\text{O}_2$).

(b) Using Phosphoric Oxide in Methanesulphonic Acid.

Phosphoric oxide (8 g) was dissolved in 98% methanesulphonic acid (45 g) at 60° and finely powdered 5-(4-methoxyphenoxy)-1*H*-*v*-triazole-4-carboxylic acid (**4c**, 1.40 g) was added. The resulting solution was stirred at 80-90° for 24 hours and then cooled and diluted with ice-water. The bulk of the acid was neutralised with dilute aqueous sodium hydroxide and the product was extracted into ethyl acetate. Evaporation of the dried (magnesium sulfate) extracts gave a brown solid which was triturated with ether and dried. Recrystallisation from ethanol after charcoal treatment yielded 0.41 g (32%) of **9c** of mp 263° dec; m/s : M^+ 217.0504 ($\text{C}_{10}\text{H}_7\text{N}_3\text{O}_3$).

1-Benzyl-5-(3-methoxyphenyl)-*v*-triazole-4-carboxylic Acid (**15**).

Hydrolysis of ester **4d**, according to the method described for compound **5** afforded a 96% yield of compound **15** of mp 130-131° dec, from ethanol-petroleum ether, (bp 40-60°).

Anal. Calcd. for $\text{C}_{17}\text{H}_{15}\text{N}_3\text{O}_4$: C, 62.75; H, 4.65; N, 12.9. Found: C, 62.45; H, 4.5; N, 12.8.

Hydrogenolysis of Compound **15**.

A solution of **15** (30.0 g, 0.092 mole) in ethanol (300 ml) was hydrogenated over palladium on charcoal (0.3 g, of 10%) at 1000 psi and 80° for 2 hours. The catalyst was removed from the cooled solution by filtration and the filtrate evaporated *in vacuo* to give 20.01 g of a mixture of 5-(3-methoxyphenoxy)-*v*-triazole-4-carboxylate (**8e**) and 1-benzyl-5-(3-methoxyphenoxy)-*v*-triazole (**16**). Extraction of this mixture with alkali gave 5.42 g (27%) of **8e** on acidification of mp 133-134°, from ethyl acetate-petroleum ether (bp 40-60°). From the neutral phase 10.24

g (39%) of 16 was recovered as a colourless oil; ir: ν max (film) 1615, 1595, 1565, 1560, 1490 cm^{-1} .

Anal. Calcd. for $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_2$: C, 68.3; H, 5.35; N, 14.95. Found: C, 68.1; H, 5.55; N, 15.05.

1-Benzyl-5-phenoxy-1*H*-*v*-triazole.

Heating 1.00 g of 1-benzyl-5-phenoxy-1*H*-*v*-triazole-4-carboxylic acid (5) at 120-130° resulted in spontaneous decarboxylation. After 30 minutes the light brown liquid was cooled, dissolved in chloroform and filtered through silica gel to give 0.48 g (94%) of the decarboxylated product of mp 47-48°, from toluene-petroleum ether (bp 40-60°); ir: ν max 1595, 1560 cm^{-1} ; ^1H -nmr (deuteriochloroform): δ 5.42 (2H, s, CH_2), 7.12 (1H, s, vinyl C-H), 7.30 (5H, s, CH_2Ph), 6.90-7.38 (5H, m, *OPh*), ms, M^+ 251.1068 ($\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}$).

Anal. Calcd. for $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}$: C, 71.7; H, 5.2; N, 16.7. Found: C, 71.7; H, 5.45; N, 16.55.

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