Studies on *v*-Triazoles. Part 4.[1] The 4-Methoxybenzyl Group, a Versatile *N*-Protecting Group for the Synthesis of *N*-Unsubstituted *v*-Triazoles

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A series of readily prepared monocyclic *N*-(4-methoxybenzyl)-*v*-triazoles (1) have been converted into their *N*-unsubstituted derivatives (2) by treatment with trifluoroacetic acid at 65 °C. The procedure allows the synthesis of a range of *N*-unsubstituted *v*-triazoles. Its applicability to multicyclic systems is demonstrated by the synthesis of 3,9-dihydro-9-oxobenzopyrano[2,3-*d*]-*v*-triazole (5b), one of a series of compounds of interest as potential antiallergic agents.

SEVERAL methods exist for the synthesis of the *v*-triazole system; the most notable are those involving the cycloaddition of azides to acetylenic compounds,[2] or the base-catalysed condensation of azides with active methylene compounds.[3] The former suffers from the limited accessibility of suitable acetylenic precursors, although a variety of azides, including the azide ion itself,[4] have been used effectively. The latter is an attractive route to *v*-triazoles bearing carbonyl functions and hydroxy- or amino-functions at positions C-4 and C-5, respectively, and is, moreover, regiospecific.[5]

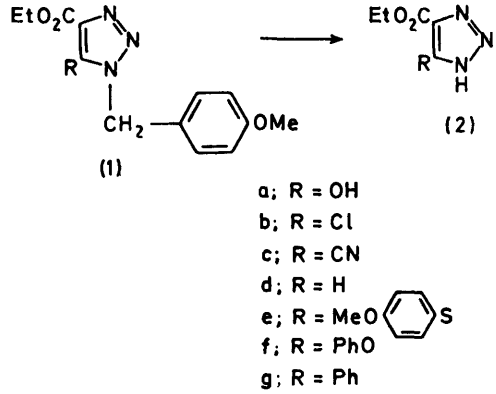
Because of its stability, benzyl azide has frequently been used in such reactions, but the difficulty of removing *N*-benzyl groups from *v*-triazoles under all but the most forcing conditions[3,6] limits its value. Other organic azides such as tropylium,[7] trimethylsilyl,[8] and tosyl[9] have had limited use, usually because of the lability of these moieties in the triazole product. Organometallic azides such as tributyltin[10] and triphenyl-lead[11] undergo cycloaddition reaction with acetylenes, but again their versatility appears limited.

Here we report the use of the 4-methoxybenzyl system as a relatively stable azide[12] which satisfies the requirements of producing an *N*-protected triazole with stability under a wide range of experimental conditions, yet with sufficient lability for deprotection to occur readily in the presence of a variety of functional groups.

RESULTS AND DISCUSSION

4-Methoxybenzyl azide can be simply prepared from the corresponding chloride by reaction with azide ion in *N*,*N*-dimethylformamide. Condensation with diethyl malonate under conditions essentially similar to those described for benzyl azide[3] resulted in the hydroxytriazole (1a), which on subsequent treatment with phosphorus pentachloride in toluene at 40 °C gave the chloro-derivative (1b) in reasonable yield.† This compound can serve as a versatile precursor of a variety of simple triazoles by virtue of its ready halogen displacement reaction with various nucleophiles. Thus reactions with CN^-, ArS^-, and ArO^-, for example, gave the corresponding triazoles (1c, e, and f), respectively.

By 1,3-dipolar addition to suitable acetylenes, 4-methoxybenzyl azide gave the expected triazoles. Thus, reaction with ethyl propiolate resulted in (1d) as the only isolated product, whereas the reaction with ethyl phenylpropiolate afforded mixtures of the two possible



SCHEME

isomeric products (1g) and (3) in approximately equal proportions.

The 4-methoxybenzyl group was readily removed by solvolysis in trifluoroacetic acid at 65 °C (Table) the other functionalities present remaining unaffected. Good yields of the *N*-unsubstituted triazoles were obtained in all cases. Furthermore, triazolecarboxylic acids [*e.g.* (4a)] were similarly cleaved without decarboxylation. As further evidence of versatility, the acid (4a)

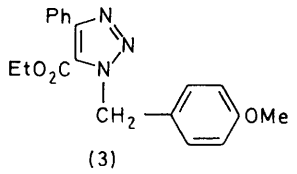
Reactions of 4-methoxybenzyl-*v*-triazoles with trifluoroacetic acid

Compound	Reaction time (h) [a]	Yield of *N*-unsubst. deriv. (%) [b]
(1a)	6	77
(1b)	3	64
(1c)	2.5	100
(1d)	6.5	67
(1e)	2.5	99 [c]
(1f)	2.5	52
(1g)	3.5	60
(3)	1.25	74
(4a)	1.5	63
(5a)	3	70

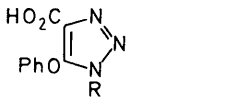
[a] Reactions were performed at an oil-bath temperature of 65 ± 2 °C and were monitored by high-pressure liquid-chromatography for optimum reaction times. [b] Yields are for purified material. [c] Characterised as its acid.

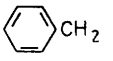
† Higher temperatures resulted in migration of the benzyl group; this will be discussed in a subsequent publication.

was converted, *via* its acyl chloride, into the tricyclic derivative (5a) which also underwent ready cleavage to the *N*-unsubstituted triazole (5b). This latter reaction represents a useful procedure for the synthesis of compounds of this type, which are of value as potential antiallergic agents,[13] especially since attempts to cleave the *N*-benzyl analogue (5c) by conventional procedures, *e.g.* hydrogenolysis, resulted in rupture of the triazole ring.[14] That the *N*-benzyl substituent is resistant to removal with trifluoroacetic acid was shown by the absence of reaction with (5c) even after 48 h at 65 °C.

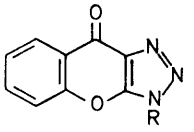


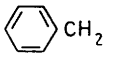
(3)



(4) a; R = MeO 

b; R = H



(5) a; R = MeO 

b; R = H

c; R = $PhCH_2$

The 4-methoxybenzyl substituent is stable under a range of standard reaction conditions, *e.g.* (*a*) hot aqueous alkali, (*b*) aqueous acid, (*c*) oxidants such as potassium permanganate, (*d*) cold Lewis acids such as aluminium chloride, (*e*) various nucleophilic reagents such as CN^-, ArS^-, ArO^-, and (*f*) mild catalytic hydrogenolysis. The value of the foregoing procedure as a general route to otherwise inaccessible or difficultly accessible *N*-unsubstituted triazoles is enhanced by virtue of the known [15] ease of decarboxylation of triazolecarboxylic acids, which themselves are readily available from the hydrolysis of esters of type (2).

EXPERIMENTAL

M.p.s were determined using a Büchi apparatus. I.r. spectra were measured for dispersions in Nujol (Perkin–Elmer 197 spectrophotometer) unless otherwise specified. N.m.r. spectra were obtained with a Varian EM 390 (90 MHz) spectrometer for solutions in the indicated solvents with Me_4Si as standard. Mass spectra were measured using a Perkin–Elmer 554 spectrometer.

4-Methoxybenzyl Azide.[12]—Sodium azide (2.15 g, 33 mmol) was stirred for 24 h at 20 °C with a solution of 4-methoxybenzyl chloride [16] (5.18 g, 33 mmol) in dry *N*,*N*-dimethylformamide (DMF) (20 ml), and the mixture was diluted with water (200 ml). The organic azide was extracted into ether and the extracts were washed well with water and dried (Na_2SO_4). Evaporation *in vacuo* (<20 °C) afforded the title azide (5.12 g, 95%) as a colourless oil, $\nu_{max.}$ (film) 2 000 cm^{-1}, which was used without further purification.

Ethyl 5-Hydroxy-1-(4-methoxybenzyl)-v-triazole-4-carboxylate (1a).—To a stirred solution of sodium ethoxide [from sodium (6.03 g, 0.26 mol)] in ethanol (450 ml) was added diethyl malonate (41.9 g, 0.26 mol). After 30 min a solution of 4-methoxybenzyl azide (42.5 g, 0.26 mol) in ethanol (50 ml) was added dropwise with stirring and the mixture was gently refluxed for 18 h. After cooling, the bulk of the ethanol was removed *in vacuo* and water was added. Acidification to pH 2 with dilute hydrochloric acid gave a crystalline precipitate, which was filtered off, washed with water, and dried *in vacuo* (P_4O_{10}). Recrystallization from chloroform–light petroleum (b.p. 40—60 °C) gave the *triazole* (1a) (47.7 g, 67%); *m.p.* 117 °C; $\nu_{max.}$ 2 350br, 1 950br, and 1 710 cm^{-1}; δ[$(CD_3)_2SO$] 1.22 (3 H, t, *J* 7.0 Hz, CH_3CH_2), 3.70 (3 H, s, CH_3O), 4.22 (2 H, q, *J* 7.0 Hz, CH_3CH_2), 5.23 (2 H, s, NCH_2), 7.03 (4 H, ABq, *J* 9 Hz, Δν 20 Hz, aromatic), and 9.20 (1 H, br, exchangeable OH) (Found: C, 56.4; H, 5.75; N, 15.0. $C_{13}H_{15}N_3O_4$ requires C, 56.3; H, 5.45; N, 15.15%).

Ethyl 5-Chloro-1-(4-methoxybenzyl)-v-triazole-4-carboxylate (1b).—Phosphorus pentachloride (30.0 g, 0.144 mol) was added to a stirred solution of the hydroxy-ester (1a) (37.0 g, 0.133 mol) in dry toluene (400 ml) and the mixture was stirred at 40 °C (oil-bath temperature) for 90 min. The solvent was removed *in vacuo* and the residue taken up in ether and washed well with saturated aqueous sodium hydrogen carbonate and then water. Evaporation of the dried ($MgSO_4$) organic phase gave an oil from which the *chloro-compound* (1b) (25.5 g, 65%), m.p. 76.5—77 °C, was isolated by crystallisation from ether–light petroleum (b.p. 40—60 °C); $\nu_{max.}$ 1 720, 1 615, 1 585, 1 537, and 1 515 cm^{-1}; δ($CDCl_3$) 1.38 (3 H, t, *J* 7 Hz, CH_3CH_2), 3.75 (3 H, s, CH_3O), 4.39 (2 H, q, *J* 7 Hz, CH_3CH_2), 5.47 (2 H, s, CH_2N), 7.03 (4 H, ABq, *J* 9 Hz, Δν 35 Hz, aromatics) (Found: C, 53.0; H, 4.9; Cl, 11.95; N, 14.1. $C_{13}H_{14}ClN_3O_3$ requires C, 52.8; H, 4.75; Cl, 12.0; N, 14.2%).

Ethyl 5-Cyano-1-(4-methoxybenzyl)-v-triazole-4-carboxylate (1c).—Sodium cyanide (0.51 g, 10.4 mmol) was added to a solution of (1b) (2.96 g, 10 mmol) in dry DMF (15 ml) and the mixture was stirred at 80 °C for 24 h. After cooling, the solvent was removed *in vacuo* and the residue was partitioned between water and ethyl acetate. The organic phase was separated, washed with water, and dried ($MgSO_4$). Evaporation gave an oil which crystallised. Recrystallisation from ethanol gave the *cyano-derivative* (1c) (1.89 g, 66%), m.p. 81—83 °C; $\nu_{max.}$ 2 240, 1 735, 1 605, 1 580, 1 535, and 1 510 cm^{-1}; δ($CDCl_3$) 1.42 (3 H, t, *J* 7.5 Hz, CH_3CH_2), 3.80 (3 H, s, CH_3O), 4.43 (2 H, q, *J* 7.5 Hz, CH_3CH_2), 5.67 (2 H, s, CH_2N), and 7.12 (4 H, ABq, *J* 9 Hz, Δν 42 Hz, aromatic) (Found: C, 58.5; H, 5.0; N, 19.45. $C_{14}H_{14}N_4O_3$ requires C, 58.75; H, 4.95; N, 19.6%).

Ethyl 1-(4-Methoxybenzyl)-v-triazole-4-carboxylate (1d).—A solution of 4-methoxybenzyl azide (5.12 g, 31 mmol) and ethyl propiolate (3.00 g, 31 mmol) in acetone (100 ml) was refluxed for 24 h, cooled, and evaporated to dryness *in vacuo*. The resulting oil crystallised on trituration with light petroleum (b.p. 40—60 °C) to give the *triazole* (1d) (3.65 g, 45%), m.p. 90—92 °C; $\nu_{max.}$ 3 145, 1 725, and 1 620 cm^{-1}; δ($CDCl_3$) 1.38 (3 H, t, *J* 7 Hz, CH_3CH_2), 3.83 (3 H, s, CH_3O), 4.42 (2 H, q, *J* 7 Hz, CH_3CH_2), 5.55 (2 H, s, CH_2N), 7.14 (4 H, ABq, *J* 9 Hz, Δν14 Hz, aromatic), and 7.99 (1 H, s, vinyl CH) (Found: C, 59.75; H, 5.5; N, 16.3. $C_{13}H_{15}N_3O_3$ requires C, 59.75; H, 5.8; N, 16.1%).

Ethyl 1-(4-*Methoxybenzyl*)-5-(4-*methoxyphenylthio*)-v-*triazole*-4-*carboxylate* (1e).—Finely powdered (1b) (20.60 g, 70 mmol) was added with stirring to a solution of the sodium salt of 4-methoxybenzenethiol [from the thiol (9.80 g, 70 mmol) and a 50% dispersion of sodium hydride in mineral oil (3.36 g, 70 mmol)] in dry DMF (150 ml), and the mixture was stirred at 80 °C for 18 h. After cooling the solvent was evaporated off *in vacuo* and the residue was partitioned between water and ethyl acetate (a small amount of insoluble disulphide was removed at this stage). The organic layer was separated, washed with dilute aqueous sodium hydroxide and water, and dried ($MgSO_4$). Evaporation afforded a white crystalline solid which was recrystallised from ethanol–light petroleum (b.p. 60—80 °C) after decolourisation to give the *product* (1e) (20.75 g, 74%), m.p. 95—96 °C; $\nu_{max.}$ 1 730, 1 615, 1 595, 1 520, and 1 500 cm^{-1}; $\delta(CDCl_3)$ 1.34 (3 H, t, *J* 7 Hz, CH_3CH_2), 3.78 (6 H, s, CH_3O), 4.37 (2 H, q, *J* 7 Hz, CH_3CH_2), 5.56 (2 H, s, CH_2N), 6.72 (2 H, d, *J* 9 Hz), 6.80 (2 H, d, *J* 9 Hz), 7.10 (2 H, d, *J* 9 Hz), and 7.13 (2 H, d, *J* 9 Hz) (Found: C, 60.35; H, 5.55; N, 10.45; S, 8.05. $C_{20}H_{21}N_3O_4S$ requires C, 60.15; H, 5.3; N, 10.5; S, 8.05%).

Ethyl 1-(4-*Methoxybenzyl*)-5-*phenoxy*-v-*triazole*-4-*carboxylate* (1f).—Sodium hydride (1.63 g, 34 mmol of a 50% dispersion in mineral oil) was added to a solution of phenol (3.18 g, 34 mmol) in dry DMF (80 ml) and the mixture was stirred at ambient temperature for 30 min to complete the formation of the sodium salt. Compound (1b) (10.0 g, 34 mmol) was added to this solution and the mixture was stirred at 70 °C for 20 h. After cooling, the solvent was removed *in vacuo* and the residue was partitioned between water and ethyl acetate. The organic phase was washed with aqueous 5% sodium hydroxide, then water, and dried ($MgSO_4$). Evaporation gave the *ester* (1f) (10.2 g, 82%), m.p. (aqueous ethanol) 62—63 °C; $\nu_{max.}$ 1 720, 1 608, 1 595, 1 570, 1 550, and 1 515 cm^{-1}; $\delta(CDCl_3)$ 1.02 (3 H, t *J* 7 Hz, CH_3CH_2), 3.70 (3 H, s, CH_3O), 4.12 (2 H, q, *J* 7 Hz, CH_3CH_2), 5.33 (2 H, s, NCH_2), and 6.98 (9 H, m, aromatic) (Found: C, 64.3; H, 5.55; N, 12.0. $C_{19}H_{19}N_3O_4$ requires C, 64.6; H, 5.4; N, 11.9%).

Ethyl 1-(4-*Methoxybenzyl*)-5-*phenyl*-v-*triazole*-4-*carboxylate* (1g) *and Ethyl* 1-(4-*Methoxybenzyl*)-4-*phenyl*-v-*triazole*-5-*carboxylate* (3).—A mixture of 4-methoxybenzyl azide (1.00 g, 6.1 mmol) and ethyl phenylpropiolate (1.07 g, 6.1 mmol) was stirred at 95 °C for 6 h and cooled. Chromatography of the residue on silica with dichloromethane gave first the 5-*carboxylate* (3) (0.79 g, 38%), m.p. 95—96 °C; $\nu_{max.}$ 1 710 and 1 610 cm^{-1}; $\delta(CDCl_3)$ 1.22 (3 H, t, *J* 6 Hz, CH_3CH_2), 3.82 (3 H, s, CH_3O), 4.30 (2 H, q, *J* 6 Hz, CH_3CH_2), 5.94 (2 H, s, CH_2N), 7.13 (4 H, ABq, *J* 9 Hz, Δν 45 Hz), and 7.60 (5 H, m) (Found: C, 67.5; H, 5.7; N, 12.55. $C_{19}H_{19}N_3O_3$ requires C, 67.65; H, 5.7; N, 12.45%), then the 4-*carboxylate* (1g) (0.61 g, 30%), an oil; $\nu_{max.}$ (film) 1 720 and 1 610 cm^{-1}; $\delta(CDCl_3)$ 1.22 (3 H, t, *J* 7 Hz, CH_3CH_2), 3.73 (3 H, s, CH_3O), 4.22 (2 H, q, *J* 7 Hz, CH_3CH_2), 5.35 (2 H, s, CH_2N), 6.82 (4 H, ABq, *J* 9 Hz, Δν 16.5 Hz), and 7.25 (5 H, m) (Found: C, 67.75; H, 5.6; N, 12.25. $C_{19}H_{19}N_3O_3$ requires C, 67.75; H, 5.7; N, 12.45%).

1-(4-*Methoxybenzyl*)-5-*phenoxy*-v-*triazole*-4-*carboxylic Acid* (4a).—Hydrolysis of the ester (1f) (7.77 g) with an excess of aqueous 1.25M-sodium hydroxide at 70 °C over 2 h gave the *acid* (4a), isolated as a crystalline solid after acidification of the cold alkaline solution. Recrystallisation from ether–light petroleum (b.p. 40—60 °C) yielded 6.56 g (90%); m.p. 125—126 °C (decomp.); $\nu_{max.}$ 3 540, 3 300, 3 200, 2 650br, and 1 715 cm^{-1}; $\delta[(CD_3)_2SO]$ 3.73 (3 H, s, CH_3O), 5.40 (2 H, s, CH_2N), 7.07 (9 H, complex m, aromatic), and one low-field broad exchangeable OH (Found: C, 62.55; H, 4.95; N, 13.0. $C_{17}H_{15}N_3O_4$ requires C, 62.75; H, 4.65; N, 12.9%).

3,9-*Dihydro*-3-(4-*methoxybenzyl*)-9-*oxobenzopyrano*[2,3-d]-v-*triazole* (5a).—A mixture of the carboxylic acid (4a) (0.325 g, 1 mmol) and oxalyl chloride (0.254 g, 2-fold excess) in dry dichloromethane (10 ml) was treated with a catalytic amount of DMF and then stirred at ambient temperature for 1 h during which time the solution cleared. Solvent and excess of reagent were removed *in vacuo* to give the acid chloride of (4a) as a crystalline solid, $\nu_{max.}$ 1 765 cm^{-1}. This solid was redissolved in dry dichloromethane and the solution cooled to 0 °C. Anhydrous aluminium chloride (0.50 g, 3.75 mmol) was added in portions to the stirred solution over 10 min and the dark mixture stirred for a further 3 h at 0 °C. After dilution with ice–water the product was extracted into chloroform and the extracts were washed with water and brine. The dried ($MgSO_4$) extracts afforded a crystalline solid on evaporation which crystallised from ethanol to give the *product* (5a) (0.098 g, 32%), m.p. 187—189 °C (decomp.); $\nu_{max.}$ 1 685 and 1 605 cm^{-1}; $\delta[CDCl_3$—$(CD_3)_2SO]$ 3.78 (3 H, s, CH_3O), 5.64 (2 H, s, CH_2N), 6.82—7.80 (7 H, complex m, aromatic), and 8.40 (1 H, m, H-8) (Found: C, 66.25; H, 4.0; N, 13.1. $C_{17}H_{13}N_3O_3$ requires C, 66.45; H, 4.25; N, 13.65%).

General Procedure for Deprotection of Compounds (1a–g), (3), (4a), *and* (5a) *with Trifluoroacetic Acid* (TFA).—A solution of the *N*-protected triazole (*ca.* 1 g) in TFA (15—30 ml) was stirred at 60—65 °C for 1—7 h (Table); the course of the reaction was monitored by reverse-phase high-pressure liquid chromatography. The TFA was removed *in vacuo* and water was added to the residue. For compounds (1a) and (1c) evaporation of the filtered aqueous phase afforded the *N*-unsubstituted compounds (2a) and (2c), respectively, but for all other cases the product was isolated from the water-insoluble material by column chromatography with chloroform as eluant or, in the case of the acid (4b), by recrystallisation. The product yields (all of purified material) and spectroscopic and other properties were as follows.

Ethyl 5-*hydroxy*-1H-v-*triazole*-4-*carboxylate* (2a). Compound (1a) (2.00 g, 7.2 mmol) in TFA (50 ml) after 6 h at 65 °C gave (2a) (0.88 g, 77%), m.p. 134—137 °C [from ethyl acetate–light petroleum (b.p. 40—60 °C)] (lit.,[17] 145—146 °C); $\nu_{max.}$ 2 700br, 1 715, 1 650, 1 620, 1 540, and 1 218 cm^{-1}; $\delta[(CD_3)_2SO]$ 1.27 (3 H, t, *J* 7.5 Hz, CH_3), 4.22 (2 H, q, *J* 7.5 Hz, CH_2), and 11.00 (2 H, br, exchangeable OH, NH); M^+ 157.0481 ($C_5H_7N_3O_3$).

Ethyl 5-*chloro*-1H-v-*triazole*-4-*carboxylate* (2b). Compound (1b) (1.00 g, 34. mmol) in TFA (30 ml) after 3 h at 65 °C gave (2b) (0.37 g, 64%), m.p. 78—81 °C [from toluene–light petroleum (b.p. 60—80 °C)]; $\nu_{max.}$ 3 200, 3 150, 1 720, and 1 500 cm^{-1}; $\delta(CDCl_3)$ 1.48 (3 H, t, *J* 7.5 Hz, CH_3), 4.48 (2 H, q, *J* 7.5 Hz, CH_2), 13.3 (1 H, br, exchangeable NH) (Found: C, 34.05; H, 3.45; Cl, 20.2; N, 23.65. $C_5H_6ClN_3O_2$ requires C, 34.2; H, 3.45; Cl, 20.2; N,23.95%).

Ethyl 5-*cyano*-1H-v-*triazole*-4-*carboxylate* (2c). Compound (1c) (1.144 g, 4.0 mmol) in TFA (20 ml) after 2.5 h at 65 °C gave (2c) (0.58 g, 87%), m.p. 111—113 °C [from ether–light petroleum (b.p. 40—60 °C)]; $\nu_{max.}$ 3 200, 2 240, 1 715, and 1 500 cm^{-1}; $\delta[CDCl_3$–$(CD_3)_2SO]$ 1.42 (3 H, t, *J* 6 Hz, CH_3), 4.42 (2 H, q, *J* 6 Hz, CH_2), 15.0 (1 H, br, exchange-

able NH) (Found: C, 43.3; H, 3.8; N, 33.95. $C_6H_6N_4O_2$ requires C, 43.4; H, 3.65; N, 33.7%).

Ethyl 1H-v-*triazole*-4-*carboxylate* (2d). Compound (1d) (66 mg, 0.25 mmol) in TFA (2 ml) after 6.5 h at 65 °C gave (2d) (24 mg, 67%), m.p. 113—114 °C (from water) (lit.,[18] 112—113 °C); $\nu_{max.}$ 3 150 and 1 705 cm^{-1}.

Ethyl 5-(4-*methoxyphenylthio*)-1H-v-*triazole*-4-*carboxylate* (2e). Compound (1e) (2.00 g, 5 mmol) in TFA (50 ml) after 2.5 h at 65 °C gave (2e) (1.39 g, 99%), an oil; $\nu_{max.}$ (film) 3 120br, 1 715, and 1 590 cm^{-1}; $\delta(CDCl_3)$ 1.40 (3 H, t, *J* 7.5 Hz, CH_3CH_2), 3.83 (3 H, s, CH_3O), 4.42 (2 H, q, *J* 7.5 Hz, CH_2), 7.27 (4 H, ABq, *J* 9.5 Hz, $\Delta\nu$ 54 Hz, aromatic), and one broad low-field exchangeable NH; M^+ 279.0681 ($C_{12}H_{13}N_3O_3S$).

Aqueous alkaline hydrolysis of the ester (2e) gave the acid (90%), m.p. 165 °C (decomp.) [from ethyl acetate–light petroleum (b.p. 40—60 °C)]; $\nu_{max.}$ 3 100br, 2 650br, 1 680, 1 590, and 1 565 cm^{-1}; $\delta[(CD_3)_2SO]$ 3.90 (3 H, s, CH_3O), 7.35 (4 H, ABq, *J* 8.5 Hz, $\Delta\nu$ 40 Hz, aromatic), and 14.5 (2 H, br, exchangeable OH, NH) (Found: C, 47.9; H, 3.7; N, 16.7; S, 12.75. $C_{10}H_9N_3O_3S$ requires C, 47.8; H, 3.6; N, 16.7; S, 12.75%).

Ethyl 5-*phenoxy*-1H-v-*triazole*-4-*carboxylate* (2f). Compound (1f) (40 mg, 0.133 mmol) in TFA (3 ml) after 2.5 h at 65 °C gave (2f) (14 mg, 52%), m.p. 96.5—98 °C (from aqueous ethanol) (lit.,[19] 96—97 °C); $\nu_{max.}$ (KBr) 3 200, 3 030, 2 960, 1 730sh, 1 693, and 1 590 cm^{-1}; $\delta(CDCl_3)$ 1.28 (3 H, t, *J* 7 Hz, CH_3), 4.38 (2 H, q, *J* 7 Hz, CH_2), 7.01—7.50 (5 H, complex m, aromatic), and 13.0 (1 H, br, exchangeable NH).

Ethyl 5-*phenyl*-1H-v-*triazole*-4-*carboxylate* (2g). Compound (1 g) (150 mg, 0.45 mmol) in TFA (3 ml) after 3.5 h at 65 °C gave (2g) (57 mg, 60%), m.p. 93 °C (lit.,[20] 92—93 °C); $\nu_{max.}$ 1 720 cm^{-1}; $\delta[(CD_3)_2SO]$ 1.25 (3 H, t, *J* 7 Hz, CH_3), 4.27 (2 H, q, *J* 7 Hz, CH_2), and 7.60 (5 H, m, aromatics).

Compound (3) (200 mg, 0.6 mmol) in TFA (4 ml) after 1.25 h at 65 °C gave (2g) (95 mg, 74%), m.p. 93—94 °C, identical with that described above.

5-*Phenoxy*-1H-v-*triazole*-4-*carboxylic acid* (4b). Compound (4a) (150 mg, 0.46 mmol) in TFA (2 ml) after 1.5 h at 65 °C gave (4b) (55 mg, 63%), m.p. 138 °C (from water) (lit.,[14] 139—140 °C); $\nu_{max.}$ 3 130, 2 600br, 1 720, 1 700, and 1 550 cm^{-1}.

3,9-*Dihydro*-9-*oxobenzopyrano*[2,3-d]-v-*triazole* (5b). Compound (5a) (0.40 g, 1.3 mmol) in TFA (5 ml) after 3 h at 65 °C gave (5 b) (0.17 g, 70%), m.p. 250—251 °C (from ethanol) (lit.,[14] 250—251 °C); $\nu_{max.}$ 2 700br, 1 650, 1 638, 1 605, and 1 560 cm^{-1}; $\delta[(CD_3)_2SO]$ 7.70 (3 H, m, H-5, -6, and -7), and 8.28 (1 H, dd, *J* 2 and 10 Hz, H-8).

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