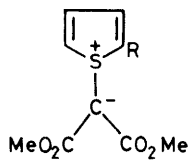
An Expeditious Synthesis of 4-Alkoxycarbonyl-5-hydroxy-1,2,3-triazoles: the Crystal and Molecular Structure of the 2-Thienylammonium Salt of 5-Hydroxy-4-methoxycarbonyl-1-(2-thienyl)-1,2,3-triazole

Peter Murray-Rust, James McManus, Sean P. Lennon, Alexander E. A. Porter,* and Josef A. Rechka
Chemistry Department, University of Stirling, Stirling FK9 4LA, Scotland

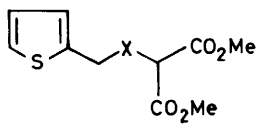
Dimethyl diazomalonate undergoes reaction with primary alkyl amines to generate the corresponding primary ammonium salts of 1-alkyl-5-hydroxy-4-methoxycarbonyl-1,2,3-triazoles; the structure of the product from the reaction of the diazoester with 2-thienylamine has been confirmed by *X*-ray methods.

We have shown[1-3] that diazomalonic esters react with thiophene and its derivatives to yield thiophenium ylides (**1**) in high yields and, as a part of our continuing interest in the chemistry of these ylides, we have sought to investigate the generality of this reaction, particularly in systems where competing side reactions might be expected.

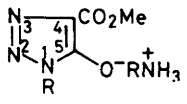
In the case of thiophene derivatives containing OH or NH_2 groups competing carbene insertion reactions might be expected to yield the malonate derivatives (**2**). In our hands, 2-hydroxymethylthiophene gave rise to the ylide (**1**; R = CH_2OH) in 54% yield although others[4] have been unable to obtain the ylide and reported the formation of the carbene insertion product (**2**; X = O). Reaction of dimethyl diazomalonate with an excess of 2-thienylamine in the presence of $Rh_2(OAc)_4$ at room temperature resulted in the slow deposition of a colourless crystalline solid and after 3 days the reaction was complete as evidenced by the disappearance of the diazo-stretching vibration in the i.r. spectrum.



(**1**)



(**2**)



(**3**)

The structure of the product proved difficult to elucidate, particularly since the mass spectrum indicated a molecular formula of $C_9H_8N_3O_3S$ whereas the microanalytical data were consistent with a molecular formula of $C_{14}H_{16}N_4O_3S_2$. The spectral data were also inconsistent with our preconceived ideas on the possible products from the reaction and the sample was thus submitted for *X*-ray crystallographic analysis.

Crystals of the product, $C_{14}H_{16}N_4O_3S_2$, M_r 352.85, were triclinic space group $P\bar{1}$, a = 10.89 (2), b = 8.41 (1), c = 10.40 (2) Å, α = 92.20 (5)°, β = 106.39 (5)°, γ = 111.40 (2)°, U = 840.7 Å^3, Z = 2, D_m = 1.394 g cm^{-3} (D_c = 1.393 g cm^{-3}), Mo-K_α radiation (λ = 0.7107A), μ = 2.86 cm^{-1}. 1 999 Reflections ($h0$—$6l$) with 0 < 25° were collected on a STADI-2 diffractometer of which 1 223 with $I > 3\sigma(I)$ were used. The structure was solved by direct methods and all hydrogen atoms were located. The full-matrix refinement with anisotropic thermal parameters for heavy atoms converged at R = 0.057.

The structure of the product (see Figure) consists of 2-thienylammonium cations hydrogen bonded to the heterocyclic anions (**3**; R = 2-thienyl). The 5-hydroxy-1,2,3-triazole system has not been structurally observed previously and the ring bond lengths (Table 1) and bond angles (Table 2) are consistent with

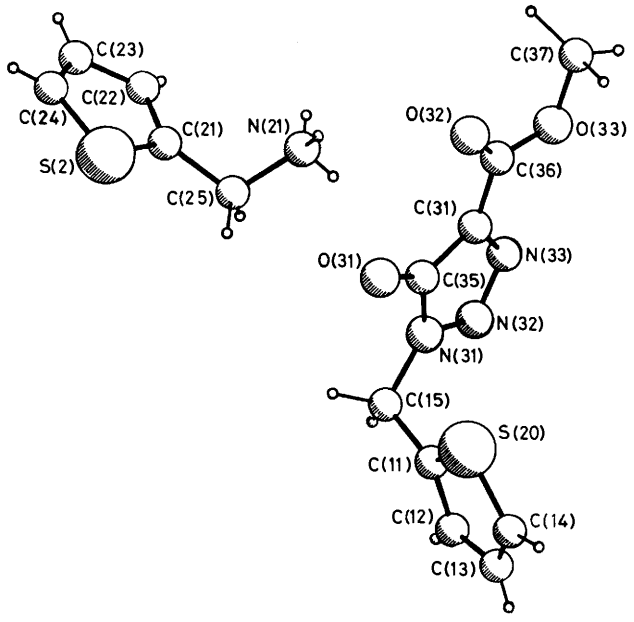


Figure.

Table 1. Bond distances (Å) with e.s.d.s in parentheses

C(11)–C(12)	1.414(9)	C(24)–S(2)	1.684(9)
C(11)–C(15)	1.503(9)	C(25)–N(21)	1.494(9)
C(11)–S(20)	1.723(7)	C(34)–C(35)	1.416(9)
C(12)–C(13)	1.429(12)	C(34)–C(36)	1.449(9)
C(13)–C(14)	1.337(12)	C(34)–N(33)	1.375(8)
C(14)–S(20)	1.699(8)	C(35)–N(31)	1.382(8)
C(15)–N(31)	1.456(8)	C(35)–O(31)	1.261(8)
C(21)–C(22)	1.413(10)	C(36)–O(32)	1.216(9)
C(21)–C(25)	1.530(10)	C(36)–O(33)	1.346(9)
C(21)–S(2)	1.700(8)	C(37)–O(33)	1.460(10)
C(22)–C(23)	1.418(13)	N(31)–N(32)	1.378(7)
C(23)–C(24)	1.316(13)	N(32)–N(33)	1.312(7)

Table 2. Bond angles (°) with e.s.d.s in parentheses

C(15)–C(11)–C(12)	126.0(7)	N(33)–C(34)–C(36)	124.5(7)
S(20)–C(11)–C(12)	113.1(6)	N(31)–C(35)–C(34)	102.0(6)
S(20)–C(11)–C(15)	120.8(5)	O(31)–C(35)–C(34)	134.7(6)
C(13)–C(12)–C(11)	106.8(7)	O(31)–C(35)–N(31)	123.2(6)
C(14)–C(13)–C(12)	117.3(8)	O(32)–C(36)–C(34)	123.2(8)
S(20)–C(14)–C(13)	111.1(8)	O(33)–C(36)–C(34)	113.0(7)
N(31)–C(15)–C(11)	112.5(5)	O(33)–C(36)–O(32)	123.8(6)
C(25)–C(21)–C(22)	127.4(7)	C(35)–N(31)–C(15)	125.5(7)
S(2)–C(21)–C(22)	113.3(6)	N(32)–N(31)–C(15)	122.4(5)
S(2)–C(21)–C(25)	119.3(7)	N(32)–N(31)–C(35)	111.8(5)
C(23)–C(22)–C(21)	107.4(9)	N(33)–N(32)–N(31)	107.3(5)
C(24)–C(23)–C(22)	115.1(10)	N(32)–N(33)–C(34)	109.2(6)
S(2)–C(24)–C(23)	113.6(8)	C(37)–O(33)–C(36)	114.6(7)
N(21)–C(25)–C(21)	110.8(6)	C(24)–S(2)–C(21)	90.6(5)
C(36)–C(34)–C(35)	125.7(7)	C(14)–S(20)–C(11)	91.7(5)
N(33)–C(34)–C(35)	109.7(6)		

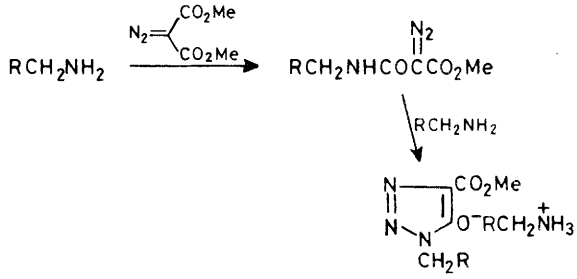
Table 3. Fractional atomic co-ordinates ($\times 10^4$) with e.s.d.s in parentheses

	x/a	*y/b*	*z/c*
C(11)	1 141(7)	3 786(11)	10 265(7)
C(12)	1 454(8)	3 715(12)	11 671(7)
C(13)	2 627(11)	5 272(16)	12 346(10)
C(14)	3 148(10)	6 392(15)	11 570(9)
C(15)	0 001(8)	2 415(12)	9 148(8)
C(21)	−3 694(7)	2 697(11)	2 909(8)
C(22)	−4 469(8)	1 108(13)	2 020(8)
C(23)	−5 562(11)	1 321(18)	1 014(12)
C(24)	−5 608(9)	2 857(17)	1 150(10)
C(25)	−2 431(9)	3 112(16)	4 174(9)
C(34)	1 332(7)	1 465(11)	6 548(7)
C(35)	0 661(7)	2 419(11)	7 010(7)
C(36)	1 806(7)	1 695(13)	5 372(8)
C(37)	3 041(16)	0 949(21)	4 081(14)
N(21)	−1 222(7)	3 044(13)	3 799(7)
N(31)	0 525(6)	1 775(8)	8 187(5)
N(32)	1 087(6)	0 550(9)	8 439(6)
N(33)	1 564(6)	0 364(9)	7 442(6)
O(31)	0 216(5)	3 547(7)	6 567(5)
O(32)	1 590(6)	2 682(8)	4 598(5)
O(33)	2 555(6)	0 760(8)	5 261(5)
S(2)	−4 335(3)	4 240(4)	2 495(3)
S(20)	2 233(3)	5 656(4)	9 900(2)
H(12A)	1 076(74)	3 284(109)	11 851(72)
H(13A)	2 888(84)	5 501(122)	13 163(96)
H(14A)	3 979(88)	7 553(128)	11 858(82)
H(15A)	−0 783(68)	2 850(96)	8 566(66)
H(15B)	−0 461(81)	1 587(121)	9 519(78)
H(21A)	−0 581(106)	3 154(137)	4 580(108)
H(21B)	−0 931(104)	4 312(164)	3 313(111)
H(21C)	−1 357(85)	2 220(146)	3 257(89)
H(22A)	−4 306(87)	0 452(142)	2 149(88)
H(23A)	−6 078(114)	0 473(169)	0 337(116)
H(24A)	−6 175(94)	2 969(123)	0 573(90)
H(25A)	−2 503(83)	2 310(130)	4 776(85)
H(25B)	−2 196(79)	4 492(131)	4 602(78)
H(37A)	3 572(128)	0 522(182)	4 219(116)
H(37B)	3 741(100)	2 124(151)	4 485(93)
H(37C)	2 194(110)	0 586(152)	2 999(111)

the enol form (**3**). A full listing of atomic co-ordinates is given in Table 3. Structure factors are available as a Supplementary Publication [SUP. No. 23856 (14 pp.)].*

The *X*-ray structure determination clearly accounts for the apparent anomaly in the mass spectral/microanalytical data in that microanalysis clearly provides the empirical formula of the salts whereas in the mass spectrum the highest mass is that due to the anion of the salt.

Mechanistically it seems probable that the 2-thienylamine reacts with the diazomalonate to form the diazoamide which then undergoes base catalysed cyclisation to the 1,2,3-triazole (see Scheme), in preference to decomposition of the diazo-ester



Scheme.

by a carbenoid mechanism. We have previously noted that rhodium(II) acetate is easily poisoned in the thiophene ylide-forming reactions and it would appear that the ammonolysis of the ester is the favoured reaction. The ring closure of diazoamides to 5-hydroxy-1,2,3-triazoles is a well studied reaction[5] first noted by Dimroth[6] and it has been established that under neutral or acidic conditions the open chain diazoamide is stable but under basic conditions rapid cyclisation to salts of the 5-hydroxy-1,2,3-triazoles occurs. Support for this rationale is two-fold. The salts of (**3**) are readily converted into the free hydroxytriazoles by acidification of an aqueous solution and extraction into dichloromethane. When the organic solvent is removed, in some cases examined, the residual hydroxytriazoles often showed a diazo stretching vibration in their i.r. spectra at 2 140 cm^{-1}. Furthermore, in the case of 1-butyl-4-methoxycarbonyl-5-hydroxy-1,2,3-triazole, all attempts to purify the triazole by distillation resulted in complete isomerisation to the diazoamide. When the resulting diazoamide was treated with butylamine, the butylammonium salt of the hydroxytriazole was immediately precipitated.

The 5-hydroxy-1,2,3-triazoles were characterised spectroscopically but generally they failed to yield good microanalytical data. In the examples reported (see Experimental section) accurate mass measurement in the mass spectra proved to be the method of choice for final characterisation. The derived diazoamides also proved troublesome in that some decomposition was observed in most cases precluding microanalysis. In addition, in some cases the diazoamides failed to give a molecular ion in the mass spectrum.

Although the cyclisation of preformed diazoamides is well known this simple 'one pot' variant using dimethyl diazomalonate has not previously been reported. It does offer some advantages in that it appears to work well with primary aliphatic amines giving high yields (Table 4) of the 5-hydroxy-1,2,3-triazole salts. Low molecular weight amines of sufficient volatility serve as both solvent and substrate in the reaction, whereas with amines of higher molecular weight or low volatility the reaction is conveniently carried out in a suitable solvent (*e.g.* toluene) using greater than a two-fold excess of the amine to diazoester. The major limitation of this reaction appears to be that aromatic amines, *e.g.* aniline, fail to react, consistent with the reduced nucleophilicity of the nitrogen in aromatic amines.

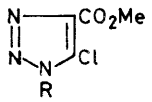
Although the free 1-alkyl-4-methoxycarbonyl-5-hydroxy-1,2,3-triazoles are unstable with respect to the diazoamides they

* For details of the Supplementary Publications Scheme see Instructions for Authors (1984) in *J. Chem. Soc., Perkin Trans. 1*, 1984, Issue 1.

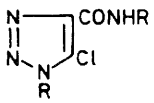
Table 4.

Amine	Reaction time (days)	Product (3)	Yield (%)
Bu^tNH_2	3	R = C_4H_9	87
n-$C_5H_{11}NH_2$	5	R = C_5H_{11}	83
n-$C_6H_{13}NH_2$	3	R = C_6H_{13}	70
Cyclohexylamine	3	R = C_6H_{11}	66
$HOCH_2CH_2NH_2$	3	R = CH_2CH_2OH	98
$PhCH_2NH_2$	3	R = CH_2Ph	84
2-Thienylamine	3	R = 2-Thienyl	67
3-Thienylamine	6	R = 3-Thienyl	72

may be chlorinated using the conditions of Buckle and Rockell;[7] thus 1-benzyl-5-hydroxy-4-methoxycarbonyl-1,2,3-triazole was converted into the 5-chloro derivative (**4**) in excellent yield. In contrast to the observations of Buckle and Rockell that the halogen atom in 1-substituted 5-chloro-1,2,3-triazoles is readily displaced by oxygen and sulphur nucleophiles, and CN^-, the reaction with nitrogen nucleophiles proved to be slow. Treatment of (**4**) with aqueous ammonia and aqueous methylamine failed to bring about substitution of the chlorine atom and the products of reaction were the amides (**5**; R = H) and (**5**; R = Me).



(**4**)



(**5**)

Experimental

M.p.s were determined on a Kofler block and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 577 instrument as KBr discs or solution spectra as indicated. N.m.r. spectra were recorded on a Perkin-Elmer R32 or Bruker WP80 instrument and mass spectra on a Jeol JMS D100.

Preparation of the Triazole Salts (**3**).—The 1,2,3-triazole salts (**3**) were prepared by two methods.

Method A. Dimethyl diazomalonate (10 mmol) was added to a large excess of the amine and the reaction was stirred at room temperature and monitored by i.r. spectroscopy until the diazoester was completely consumed. At this point the resultant salt had crystallised from solution and was isolated by filtration and crystallised.

Method B. Dimethyl diazomalonate (10 mmol) was added to a solution of the amine (20—50 mmol) in toluene (10 ml) and the reaction stirred at room temperature and monitored as above. The product was isolated by filtration and recrystallised.

1-Butyl-5-hydroxy-4-methoxycarbonyl-1,2,3-triazole butylammonium salt (**3**; R = Bu^n). Method A, yield 2.22 g (82%), m.p. (ethyl acetate) 111—113 °C, $\nu_{max.}$(KBr) 3 200—2 400, 1 690, 1 570, 1 460, and 1 415 cm^{-1}; $\delta(CDCl_3)$ 8.4 (3 H, br s), 3.9 (2 H, m), 3.65 (3 H, s), 3.9 (2 H, m), 3.65 (3 H, s), 3.0 (2 H, t), 2—1.2 (8 H, m), and 1.1—0.8 (6 H, m) (Found: C, 52.9; H, 9.05; N, 20.9. $C_{12}H_{24}N_4O_3$ requires C, 52.95; H, 8.82; N, 20.59%).

5-Hydroxy-4-methoxycarbonyl-1-pentyl-1,2,3-triazole pentylammonium salt (**3**; R = n-C_5H_{11}). Method B, yield 2.5 g (85%), m.p. 110—113 °C (CH_3CN), $\nu_{max.}$(KBr) 3 200—2 400, 1 690, 1 550, and 1 460 cm^{-1}; δ(DMSO) 8.00 (3 H, br s), 3.55 (3 H, s), and 2.5—1.0 (22 H, m) (Found: C, 56.2; H, 9.3; N, 18.45. $C_{14}H_{28}N_4O_3$ requires C, 56.00; H, 9.33; N, 18.66%).

1-Hexyl-5-hydroxy-4-methoxycarbonyl-1,2,3-triazole n-hexylammonium salt (**3**; R = n-C_6H_{13}). Method B, yield 2.3 g (70%), m.p. (methanol–acetonitrile), 120—122 °C, $\nu_{max.}$(KBr) 3 200—2 400, 1 690, 1 575, 1 460, and 1 160 cm^{-1}; $\delta[(CD_3)_2SO]$ 8.0 (3 H, s), 4.00 (3 H, s), and 3.0—1.0 (26 H, m) (Found: C, 58.6; H, 9.7; N, 16.95. $C_{16}H_{32}N_4O_3$ requires C, 58.54; H, 9.76; N, 17.07%).

1-Cyclohexyl-5-hydroxy-4-methoxycarbonyl-1,2,3-triazole cyclohexylammonium salt (**3**; R = C_6H_{11}). Method B, yield 2.14 g (66%), m.p. (CH_3CN–MeOH), 154—157 °C, $\nu_{max.}$(Nujol) 3 200—2 400, 1 690, 1 575, 1 450, 1 410, 1 325, 1 165, and 1 050 cm^{-1}; $\delta[(CD_3)_2SO]$ 7.0 (3 H, br s), 3.6 (3 H, s), and 3—1.0 (22 H, m) (Found: C, 59.3; H, 8.7; N, 17.3. $C_{16}H_{28}N_4O_3$ requires C, 59.26; H, 8.64; N, 17.28%).

5-Hydroxy-1-(2-hydroxyethyl)-4-methoxycarbonyl-1,2,3-triazole 2-hydroxyethylammonium salt (**3**; R = CH_2CH_2OH). Method B, yield 2.45 g (98.7%), m.p. (ethanol) 199—124 °C (decomp.), $\nu_{max.}$(KBr) 3 500—2 500, 1 700, 1 630, 1 580, 1 530, and 1 450 cm^{-1}; $\delta[(CD_3)_2SO]$ 5.5 (3 H, br s), and 3.7—3.2 (11 H, m) (Found: C, 38.65; H, 6.65; N, 22.85. $C_8H_{16}N_4O_5$ requires C, 38.71; H, 6.45; N, 22.58%).

1-Benzyl-5-hydroxy-4-methoxycarbonyl-1,2,3-triazole benzylammonium salt (**3**; R = CH_2Ph). Method B, yield 2.68 g (84%), m.p. (ethanol) 153—156 °C (decomp.), $\nu_{max.}$(KBr) 3 200—2 500, 1 960, 1 690, 1 580, 1 520, 1 460, and 1 410 cm^{-1}; $\delta(CDCl_3)$, 7.2 (5 H, s), 7.1 (5 H, s), 5.05 (2 H, s), 3.95 (2 H, s), and 3.7 (3 H, s) (Found: C, 63.5; H, 5.9; N, 16.65. $C_{18}H_{20}N_4O_3$ requires C, 63.53; H, 5.88; N, 16.47%).

5-Hydroxy-4-methoxycarbonyl-1-(2-thienyl)-1,2,3-triazole 2-thienylammonium salt (**3**; R = 2-thienyl). Method B, yield 2.36 g (67%), m.p. (acetonitrile–methanol) 160—161 °C (decomp.), $\nu_{max.}$(KBr) 3 650—3 250, 3 150—2 700, 1 690, 1 640, 1 610, 1 520, and 1 460 cm^{-1}; $\delta[(CD_3)_2SO]$ 8.7 (3 H, br s), 7.2—7.5 (3 H, m), 7.9—6.8 (3 H, m), 5.2 (2 H, s), 4.25 (2 H, s), and 3.6 (3 H, s) (Found: C, 47.65; H, 4.6; N, 15.95. $C_{14}H_{16}N_4O_3S_2$ requires C, 47.72; H, 4.55; N, 15.91%).

5-Hydroxy-4-methoxycarbonyl-1-(3-thienyl)-1,2,3-triazole 3-thienylammonium salt (**3**; R = 3-thienyl). Method B, yield 72%, m.p. (acetonitrile) 160—162 °C (decomp.), $\nu_{max.}$(KBr) 3 200—2 500br, 1 690, 1 645, 1 620, 1 550, 1 460, 1 410, and 1 320 cm^{-1}; $\delta[(CD_3)_2SO]$ 7.65 (3 H, br s), 7.4—6.7 (6 H, m), 4.8 (2 H, s), 3.85 (2 H, s), and 3.50 (3 H, s) (Found: C, 47.5; H, 4.45; N, 16.06. $C_{14}H_{16}N_4O_3S_2$ requires C, 47.59; H, 4.82; N, 15.86%).

Preparation of the 5-Hydroxy-4-methoxycarbonyl-1,2,3-triazoles.—In general the hydroxytriazoles were prepared by stirring the corresponding alkyl ammonium salts (1 g) in 1M-HCl (5 ml) for 15 min followed by extraction into dichloromethane (2 × 10 ml). The extracts were dried over $MgSO_4$, filtered, and evaporated. The yields were generally quantitative.

5-Hydroxy-4-methoxycarbonyl-1-(2-thienyl)-1,2,3-triazole, m.p. (dichloromethane) 104—106 °C, $\nu_{max.}$(KBr) 2 950, 1 725, 1 600, 1 530, 1 460, 1 410, and 1 330 cm^{-1}; $\delta[CDCl_3$–$(CD_3)_2SO]$ 7.3—6.9 (3 H, m), 5.5 (2 H, s), and 3.9 (3 H, s) (Found: M^+, 239.0374. $C_9H_9N_3O_3S$ requires M, 239.0365).

5-Hydroxy-4-methoxycarbonyl-1-(3-thienyl)-1,2,3-triazole, viscous oil, $\nu_{max.}$(film) 3 090, 2 960, 2 500—2 300br, 1 720, 1 600, 1 530, and 1 450 cm^{-1}; $\delta(CDCl_3)$ 7.3—7.0 (3 H, m), 5.3 (2 H, s), 4.3 (1 H, s), and 3.85 (3 H, s) (Found: M^+, 239.0367. $C_9H_9N_3O_3S$ requires M, 239.0365).

1-Butyl-5-hydroxy-4-methoxycarbonyl-1,2,3-triazole, oil, $\nu_{max.}(CHCl_3)$ 3 300br, 2 980, 2 140w, 1 720, 1 590, 1 550, and 1 460 cm^{-1}; δ(CDCl) 4.2 (3 H, m), 3.65 (3 H, s), 3.4 (2 H, q), and 2.0—0.7 (5 H, m) (Found: M^+, 199.0953. $C_8H_{13}N_3O_3$ requires M, 199.0957).

1-Benzyl-5-hydroxy-4-methoxycarbonyl-1,2,3-triazole, m.p. (CH_2Cl_2) 109—111 °C, $\nu_{max.}$(KBr) 3 010, 1 690, 1 600, 1 530, 1 450, and 1 290 cm^{-1}; $\delta(CDCl_3)$ 7.2 (5 H, s), 5.25 (2 H, s), and

3.8 (3 H, s) (Found: M^+, 233.0791. $C_{11}H_{11}N_3O_3$ requires M, 233.0800).

1-(2-Hydroxyethyl)-4-methoxycarbonyl-5-hydroxy-1,2,3-triazole was obtained by passing an aqueous solution of the salt through an Amberlite IR120 (H^+) ion exchange column, followed by evaporation of the water, m.p. (H_2O) 109—114 °C, $\nu_{max.}$(KBr) 3 320br, 2 970, 1 720, 1 660, 1 520, 1 450, 1 390, and 1 280 cm^{-1}; δ[$(CD_3)_2SO$] 4.3 (2 H, t), 3.95 (2 H, t), and 3.9 (3 H, s) (Found: M^+, 187.0585. $C_6H_9N_3O_4$ requires M, 187.0593).

Preparation of the Diazomalonamides.—The diazomalonamides were prepared from the corresponding 5-hydroxy-1,2,3-triazoles by briefly heating them at 100 °C (2—3 min) followed by high vacuum distillation of the resultant oils at 0.1—0.05 Torr in a Kugelrohr distillation apparatus with a pre-set oven temperature of 150—180 °C. There was some decomposition of the starting material in all cases, but the products were all chromatographically homogeneous.

2-Methoxycarbonyl-*N*-(2-thienyl)-2-diazoacetamide, yield 42%, $\nu_{max.}$(film) 3 350, 3 100, 2 980, 2 140, 1 700, 1 650, 1 530, and 1 440 cm^{-1}; δ($CDCl_3$) 8.1 (1 H, br), 7.3 (1 H, m), 7.0 (2 H, m), 4.8 (2 H, d), and 3.9 (3 H, s). This product did not give a molecular ion in the mass spectrum and failed to yield consistent microanalytical data.

2-Methoxycarbonyl-*N*-(3-thienyl)-2-diazoacetamide, yield 47%, $\nu_{max.}$(film) 3 350, 3 100, 2 950, 2 140, 1 690, 1 640, 1 540, and 1 440 cm^{-1}; δ($CDCl_3$) 7.9 (1 H, br), 7.2 (3 H, m), 4.5 (2 H, d), and 3.8 (3 H, s). This product gave a mass spectral fragmentation pattern similar to the isomeric 2-thienylamide (above) with peaks at m/z 211 (35), 181 (75.0), and 97 (100%) but failed to yield a molecular ion.

N-Butyl-2-methoxycarbonyl-2-diazoacetamide, yield 71%, $\nu_{max.}$(film) 3 360, 2 960, 2 140, 1 700, 1 660, 1 540, 1 440, and 1 330 cm^{-1}; δ($CDCl_3$) 7.6 (1 H, br s), 4.15 (1 H, t), 3.8 (3 H, s), 3.3 (2 H, m), 1.5 (4 H, m), and 0.9 (3 H, m) (Found: M^+, 190.0950. $C_8H_{13}N_3O_3$ requires M, 199.0952).

N-(2-Hydroxyethyl)-2-methoxycarbonyl-2-diazoacetamide, yield 53% as an oil, $\nu_{max.}$(film) 3 350, 2 960, 2 140, 1 700, 1 640, 1 540, and 1 440 cm^{-1}; δ($CDCl_3$) 8.0 (1 H, br s), 3.9 (3 H, s), 3.75 (2 H, t), and 2.85 (1 H, s) (Found: M^+, 187.0597. $C_6H_9N_3O_4$ requires M, 187.0594).

N-Benzyl-2-methoxycarbonyl-2-diazoacetamide, yield 57% as an oil, $\nu_{max.}$(film) 3 356, 2 950, 2 130, 1 690, 1 645, 1 525, and 1 440 cm^{-1}; δ($CDCl_3$) 8.0 (1 H, br s), 7.15 (5 H, s), 3.45 (2 H, d), and 3.6 (3 H, s) (Found: M^+, 233.0806. $C_{11}H_{11}N_3O_3$ requires M, 233.0800).

1-*Benzyl*-5-*chloro*-4-*methoxycarbonyl*-1,2,3-*triazole* (**4**). 1-Benzyl-5-hydroxy-4-methoxycarbonyl-1,2,3-triazole (1.0 g) was stirred in dry toluene (40 ml) at 40 °C and to the suspension was added PCl_5 (0.95 g); the reaction mixture was then stirred at 40 °C for 90 min. The toluene was removed under reduced pressure and the residue was dissolved in ether (25 ml); saturated aqueous sodium hydrogen carbonate (25 ml) was then added. The mixture was stirred at room temperature for 15 min and the ether layer separated, dried, and evaporated to yield a pink solid which crystallised from ether–light petroleum (b.p. 40—60 °C) (1:1) to yield (**4**) as off-white needles (1.02 g, 95%), m.p. 77—79 °C, $\nu_{max.}$($CHCl_3$) 3 000, 1 725, and 1 450 cm^{-1}; δ($CDCl_3$) 7.2 (5 H, s), 5.45 (2 H, s), and 3.85 (3 H, s) (Found: C, 52.8; H, 4.0; N, 16.75. $C_{11}H_{10}ClN_3O_2$ requires C, 52.48; H, 4.0; N, 16.70%).

1-*Benzyl*-5-*chloro*-4-N-*methylcarboxamido*-1,2,3-*triazole* (**5**; R = Me). The chlorotriazole (**4**) (0.25 g) was stirred at room temperature with 40% aqueous methylamine (5 ml) for 2 h. After this time the solvent was removed under reduced pressure to yield (**5**; R = Me) (0.15 g, 60%), m.p. (MeOH–Et_2O) 149—150.5 °C, $\nu_{max.}$($CHCl_3$) 3 410, 1 665, and 1 565 cm^{-1}; δ($CDCl_3$) 7.3 (5 H, s), 5.5 (2 H, s), and 3.05 (3 H, d) (Found: M^+, 250.0626. $C_{11}H_{11}ClN_4O$ requires M, 250.0622).

1-*Benzyl*-4-*carboxamido*-5-*chloro*-1,2,3-*triazole* (**5**; R = H). To a solution of (**4**) (0.5 g) in MeOH (10 ml) was added an excess of aqueous ammonia (d 0.880) and the resultant mixture stirred for 48 h. The white solid which formed during the reaction was isolated by filtration and was dried *in vacuo* to yield (**5**; R = H) (0.31 g, 63%), m.p. (MeOH–Et_2O) 164—166 °C, $\nu_{max.}$($CHCl_3$) 3 400, 1 665, and 1 565 cm^{-1}; δ[$CDCl_3$–$(CD_3)_2SO$] 7.3 (5 H, s) and 5.5 (2 H, s) (Found: M^+, 236.0456. $C_{10}H_9ClN_4O$ requires M, 236.0465).

Acknowledgements

We thank the Cancer Research Campaign (to S. P. L.) and the S.E.R.C. (to J. A. R.) for their support of this work.

References

1 R. J. Gillespie, J. Murray-Rust, P. Murray-Rust, and A. E. A. Porter, *J. Chem. Soc., Chem. Commun.*, 1978, 83.
2 R. J. Gillespie, A. E. A. Porter, and W. E. Willmott, *J. Chem. Soc., Chem. Commun.*, 1978, 85.
3 R. J. Gillespie and A. E. A. Porter, *J. Chem. Soc., Perkin Trans 1*, 1979, 2624.
4 A. W. Taylor, Beecham Pharmaceuticals, Brockham Park, personal communication.
5 B. R. Brown and D. L. L. Hammick, *J. Chem. Soc.*, 1947, 1384.
6 O. Dimroth, *Ann*, 1910, **377**, 127.
7 D. R. Buckle and C. J. M. Rockell, *J. Chem. Soc., Perkin Trans. 1*, 1982, 627.

Received September 8th, 1983; *Paper* 3/1569