Tetrahedron Vol. 47, No. 16/17, pp. 2861-2870, 1991
Printed in Great Britain

0040-4020/91 $3.00+.00

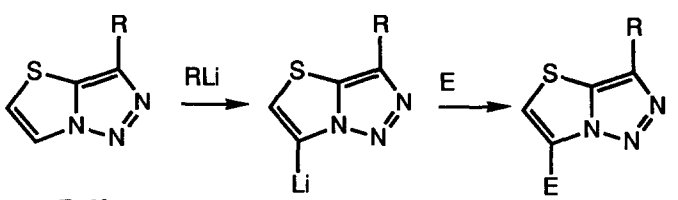
1,2,3-TRIAZOLO[5,1-b]THIAZOLES. PART 2[1] LITHIATION EXPERIMENTS LEADING TO 2,4-DISUBSTITUTED THIAZOLES

Gurnos Jones* and Hermione Ollivierre
Department of Chemistry,
University of Keele,
Keele, Staffordshire, ST5 5BG
L.S. Fuller and J.H. Young
Shell Synthetic Chemicals Ltd.,
Four Ashes, Nr. Wolverhampton, WV10 7BP

(*Received in UK* 30 *November* 1990)

3-Methyltriazolothiazole (2) and 3-phenyltriazolothiazole (3) were regiospecifically lithiated at position 6, triazolothiazole (1) at position 6 and 3 with the former predominating. The lithiated triazolothiazoles (4), (10) and (11) reacted with a number of electrophiles to give x:6-disubstituted triazolothiazoles, which could be converted into 2,4-disubstituted thiazoles.

In the previous paper[1] we reported the synthesis and some properties of the new heterocycles 1,2,3-triazolo[5,1-b]thiazole (1) and its 3-methyl- (2) and 3-phenyl- (3) derivatives. Our objective was to substitute these triazolothiazoles in a regiospecific manner, and to convert these substituted triazolothiazoles into 2,4-disubstituted thiazoles, a process which is described in this paper. Since electrophilic substitution of thiazole occurs preferentially at position 5, there is some value in a process in which electrophiles are regiospecifically introduced into position 4.[2] The lithiation of thiazole proceeds preferentially at position 2;[3] if there is a methyl group at position 2 lithiation proceeds to almost the same degree at position 5 and at the methyl group, so that 2,4-disubstitution is again not easily achieved.



Eq. 1

1 R=H
2 R=Me
3 R=Ph

E=Electrophile

The 3-substituted triazolothiazoles are discussed first, since they possess fewer potential lithiation sites on the thiazole ring. Lithiation conditions examined are listed in Table 1; in each case samples were quenched with D_2O and

the change in integration of signals due to ring protons was monitored by ^{1}H n.m.r. spectroscopy.

Table 1

Material	Lithiating Agent	Solvent	Temp. (°C)	Time (h.)	% Replacement H5	% Replacement H6
(2)	LDA	Ether	-50	10.5	0	0
(2)	n-BuLi	Ether	-35	0.16	0	100
(2)	n-BuLi	Toluene	-35	22.5	0	66
(2)	n-BuLi	THF	-35	0.5	25	75
(3)	n-BuLi	Dioxan	-10	4	0	100
(3)	n-BuLi	Toluene	20	5 min.	0	100

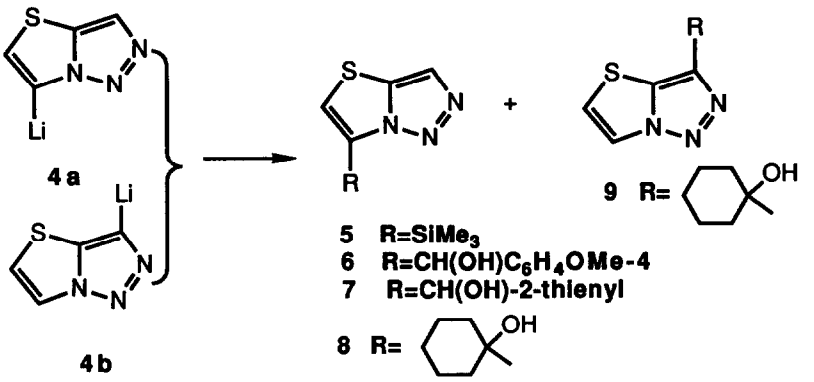
Interesting points are the strong solvent effects and the absence of detectable lithiation on the methyl group of compound (2) or on the phenyl group of compound (3). The parent triazolothiazole (1) gave less satisfactory results in deuteration experiments. Mixtures were always obtained, as shown in Table 2, but treatment of the apparent mixture of lithiated triazolothiazoles (4a) and (4b) gave in most cases as isolatable products only the 6-substituted derivatives. With satisfactory lithiation conditions available, a number of reactions with electrophiles were performed.

Table 2 Lithiation Experiments on Compound (1) using n-Butyllithium

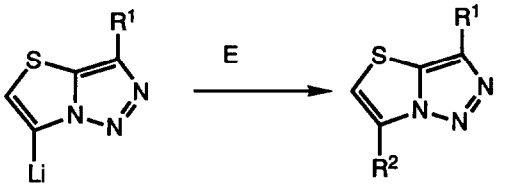
Solvent	Temp (°C)	Time (h.)	% Substitution H3	% Substitution H6
Ether	-35	0.16	50	50
Toluene	-50	3.5	33	66
Toluene	-35	1	50	50

When the lithiated triazolothiazole mixture (4a) and (4b) was treated with trimethylsilylchloride only the 6-trimethylsilyltriazolothiazole (5) was isolated, in 52% yield. Anisaldehyde gave p-methoxyphenyl(triazolothiazol-6-yl)methanol (6) in 54% yield. The 6-substituted triazolothiazoles, like the corresponding 7-substituted triazolopyridines were relatively unstable; 2-thienylcarboxaldehyde gave the alcohol (7), characterized by its spectra, but too unstable for purification for microanalysis. These three compounds showed the characteristic singlet in their ^{1}H n.m.r. spectra at δ7.65-7.8 (H3) and a second singlet at δ6.95-7.25 due to H5. When the lithioderivative (4) was treated with cyclohexanone a mixture of two products was obtained, the n.m.r. spectrum of the mixture showing that it was a 3:1 mixture of the 6-substituted (8) and 3-

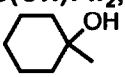
substituted triazolothiazole (9). The mixture could not be separated, but was converted into a mixture of thiazoles as described subsequently, and these were satisfactorily characterized.

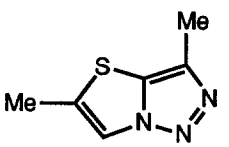


Substitution of the lithio derivatives (10) and (11) from triazolothiazoles (2) and (3) was more satisfactory. Thus compound (10) reacted with trimethylsilylchloride, benzaldehyde, anisaldehyde, thiophen-2-carboxaldehyde, benzophenone, and cyclohexanone, giving products (12)-(17). The lithio derivative (11) reacted with trimethylsilyl chloride, with anisaldehyde, with thiophen-2-carboxaldehyde, and with cyclohexanone to give products (19) - (22); of these compounds (19) and (21) were characterized spectroscopically. The lithio derivatives (4), (10) and (11) have a low level of reactivity. Attempts were made to react compound (10) with N-formylmorpholine, with ethyl chloroformate and with N,N-dimethylcarbamoyl chloride, but no products were obtained, in contrast with our experiments with triazolopyridine[4-6] The methylation of compound (10) failed in ether, but alkylation was achieved when methyl iodide in THF was added to the lithio derivative (10) in ether. The use of THF, even as co-solvent, led to isomerization, and the crude mixture of methylated products showed the presence of 3,5-dimethyl- (23) and 3,6-dimethyltriazolothiazole (18), but only the latter could be isolated and characterized spectroscopically.

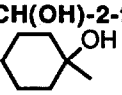


10 R^1=Me
11 R^1=Ph

12 R^1=Me, R^2=$SiMe_3$, 89%
13 R^1=Me, R^2=CH(OH)Ph, 85%
14 R^1=Me, R^2=$CH(OH)C_6H_4OMe$-4, 95%
15 R1=Me, R2=CH(OH)-2-thienyl, 77%
16 R^1=Me, R^2=$C(OH)Ph_2$, 98%
17 R^1=Me, R^2=  , 54%

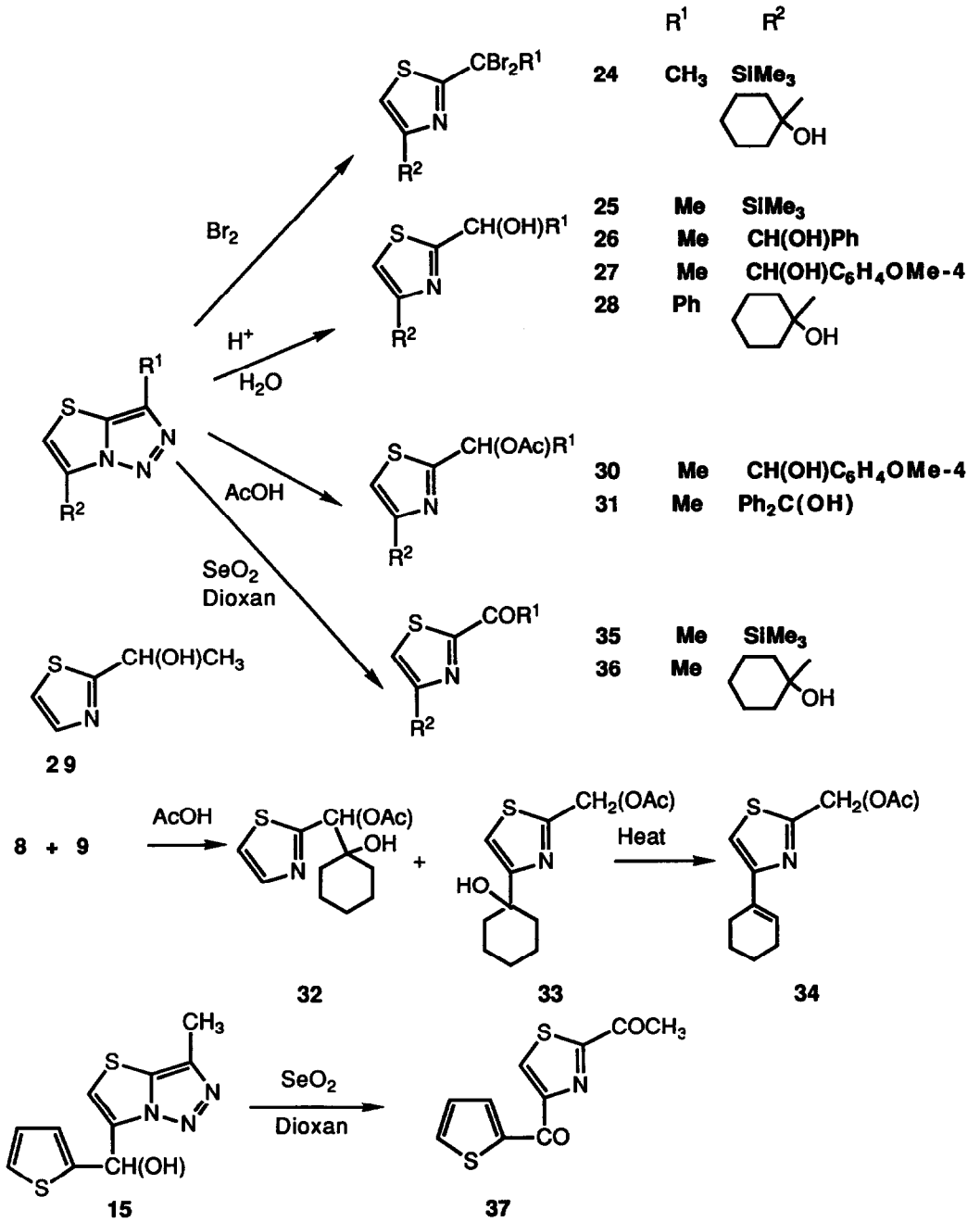


23

18 R^1=R^2=Me, 31%
19 R^1=Ph, R^2=$SiMe_3$, 44%
20 R^1=Ph, R^2=$CH(OH)C_6H_4OMe$-4, 64%
21 R^1=Ph, R^2=CH(OH)-2-thienyl, 85%
22 R^1=Ph, R^2=  , 85%

The essential feature of our project was that the triazolothiazoles, regiospecifically substituted, should be converted simply and in high yield into 2,4-disubstituted thiazoles. We have established[1] that compounds (1) - (3) undergo such reactions, and we have submitted a number of the substituted triazolothiazoles to our established ring opening procedures. The triazolothiazole (12) reacted with bromine in dichloromethane to give the 2-dibromoethylthiazole (24) in 70% yield. There was no indication of replacement of the trimethylsilyl group by bromine, but we have noted in the triazolopyridine series that a trimethylsilyl group adjacent to nitrogen is resistant to electrophilic substitution. Hot dilute sulphuric acid converted triazolothiazole (12) into the thiazolylethanol (25) in 54% yield; the crude product showed the presence of some 1-(2-thiazolyl)ethanol (29) formed by protodesilylation. The triazolothiazoles (13), (14), and (22) similarly gave thiazoles (26)-(28) in yields of 70, 83, and 71% respectively. Boiling glacial acetic acid converted triazolothiazoles (14) and (16) into the acetoxyethylthiazoles (30) and (31) in 70 and 83% yield respectively. Similar treatment of the mixture of triazolothiazoles (8) and (9) obtained from the parent triazolothiazole gave a mixture of thiazoles (32) and (33); distillation of compound (33) caused dehydration, giving the cyclohexenylthiazole (34) which gave correct microanalytical and spectroscopic data. An estimate of the efficiency of the ring opening process of 63% was obtained for compound (34). Finally, compounds (12) and (17) were treated with selenium dioxide in boiling dioxan, to give the thiazoles (35) and (36) in better

than 90% yield. As expected similar treatment of the secondary alcohol (15) with selenium dioxide gave the diketone (37) in 63% yield. We have therefore established effectively regiospecific substitution by electrophiles at position 4 of thiazoles already carrying a substituent at position 2.



EXPERIMENTAL

M.p.s. were determined on a Kofler heated stage and are uncorrected. Chromatography on the Chromatotron used 0.2 mm silica (Merck PF_{254}) with petrol/ethyl acetate as eluent. N.m.r. spectra were determined on $CDCl_3$ solutions. All lithiations were conducted under an oxygen free argon atmosphere. Off resonance ^{13}C multiplicities are given for ^{13}C signals thus (q).

Standard Procedure for Lithiation; A solution of the triazolothiazole (1 g.) in the appropriate anhydrous solvent (150 ml.; toluene for compounds (1) and (3), ether for compound (2)), was added with vigorous stirring to a cooled (-35 to -40°C) solution of n-butyllithium (1.1 molar equivalents of a 1.7 M solution in hexane, diluted with 50 ml of the cosolvent). Stirring was continued at -35°C for 1 hr. with compound (1) and 10 minutes with compound (2). Formation of the lithioderivative of compound (3) was virtually instantaneous. After addition of the coreagent (1.1 molar equivalents for compounds (1) and (2); compound (3) required 2.2 molar equivalents for the best results) the mixture was allowed to come to room temperature over night, then treated with a saturated solution of ammonium chloride in aqueous ammonia (s.g. 0.880). Extraction with dichloromethane, treatment of the extracts with anhydrous sodium sulphate, filtration, and evaporation, gave the crude product. Purification procedures are indicated for each compound.

6-Trimethylsilyltriazolothiazole (5). - Crude product was recrystallized from petrol (b.p. 40-60°C) to give pure compound (5), m.p. 118-120°C (52%). (Found: C, 42.55; H, 5.55; N, 21.3. $C_7H_{11}N_3SSi$ requires C, 42.6; H, 5.6; N, 21.3%). $\delta(^1H)$ 0.48 (9H, s), 7.19 (1H, s, H5), 7.8 (1H, s, H3). $\delta(^{13}C)$ - 2.47(q), 122.84 (d, C5), 125.91 (d, C3), 134.87 (s, C6), 137.98 (s, C3a). m/z 197 (M^+, 12%), 169 (M^+-N_2, 11%), 73 (100%).

p-Methoxyphenyl(triazolothiazol-6-yl)methanol (6). - Purification by Chromatotron (9:1) gave the alcohol (6) in 54% yield, m.p. 138-139°C (ethanol). Found: C, 55.3; H, 4.4; N, 15.6. $C_{12}H_{11}N_3SO_2$ requires C, 55.15; H, 4.2; N, 16.1%). $\delta(^1H)$ 3.8 (3H, s), 6.1-6.3 (1H, br, OH), 6.75 (1H, s, CHOH), 6.93 (2H, d, H2' and H6', J=8 Hz), 7.25 (1H, s, H5), 7.48 (2H, d, H3' and H5', J=8 Hz), 7.8 (1H, s, H3). m/z 261 (M^+, 44%), 233 (M^+-N_2, 33%), 137 (4-$MeOC_6H_4CHOH^+$, 100%).

2-Thienyl(triazolothiazol-6-yl)methanol (7). - Not purified by HPLC or by Chromatotron, the crude product showed a clean ^1H n.m.r. spectrum. δ4.9 (1H, br, OH), 6.55 (1H, s, CHOH), 6.9-7.05 (1H, m, H3'), 6.95 (1H, s, H5), 7.15-7.3 (2H, m, H2' and H4'), 7.65 (1H, s, H3). m/z 237 (M^+, 3%), 209 (M^+-N_2, 17%), 111 ($C_4H_3S.CO$, 56%), 84 (100%).

1-(Triazolothiazol-6-yl)cyclohexanol (8) and 1-(Triazolothiazol-3-yl)cyclohexanol (9). The crude mixture (1.3 g.) was analysed by ^1H n.m.r. showing signals (in the ratio of 3:1) for compound (8) at δ1.4-2.3 (10H, m, cyclohexane), 4.8

(1H, br, OH), 7.05 (1H, s, H5), and 7.7 (1H, s, H3) and for compound (9) at δ1.4-2.3 (10H, m, cyclohexane), 7.1 (1H, d, H6, J=4 Hz), and 7.85 (1H, d, H5, J=4 Hz). Further characterization was provided by treatment of the mixture with boiling glacial acetic acid, as described below.

3-Methyl-6-trimethylsilyltriazolothiazole (12). - Purified by recrystallization from petrol (b.p. 40-60°C) in 91% yield, the compound (12) had m.p. 122-122.5°C. (Found: C, 45.45; H, 6.3; N, 19.85. $C_8H_{13}N_3SSi$ requires C, 45.5; H, 6.15; N, 19.9%). δ(^{1}H) 0.4 (9H, s), 2.4 (3H, s), 7.0 (1H, s, H5). δ(^{13}C) - 2.36 (q), 11.11 (q), 125.59 (d, C5), 131.9 (s, C3), 135.2 (s, C3a), 135.41 (s, C6). m/z 211 (M^+, 10%), 183 (M^+-N_2, 24%), 73 (Me_3Si^+, 100%).

(3-Methyltriazolothiazol-6-yl)phenylmethanol (13) - Crystallized from ether, the alcohol (13) had m.p. 124-126°C (88%). (Found: C, 59.05; H, 4.6; N, 17.0. $C_{12}H_{11}N_3SO$ requires C, 58.8; H, 4.5; N, 17.15%). δ(^{1}H) 2.4 (3H, s), 6.15 (1H, br, OH), 6.7 (1H, s, H5), 7.25 (5H, s, C_6H_5). m/z 217 (M^+-N_2, 98%), 216 (M^+-N_2H, 40%), 140 (83%), 139 (30%), 138 (54%), 112 (100%), 111 (95), 77 ($C_6H_5^+$, 58%).

4-Methoxyphenyl(3-methyltriazolothiazol-6-yl)methanol (14). - Crystallized from cyclcohexane, the alcohol (14) had m.p. 141-142°C (95%). (Found: C, 57.0; H, 4.85; N, 14.85. $C_{12}H_{11}N_3SO$ requires C, 56.75; H, 4.75; N, 15.25%). δ(^{1}H) 2.35 (3H, s), 3.75 (3H, s), 4.55 (1H, br, OH), 6.1 (1H, s, CHOH), 6.65 (1H, s, H5), 6.83 (2H, d, H2' and H6', J=9 Hz), 7.38 (2H, d, H3' and H5', J=9 Hz). m/z 275 (M^+, 24%), 247 (M^+-N_2, 100%), 137 (99%), 111 (80%), 109 (42%).

2-Thienyl(3-methyltriazolothiazol-6-yl)methanol (15). - Crude product was purified by Chromatotron (5:1), giving the alcohol (15) (77%), m.p. 137-139° (cyclohexane). (Found: C, 47.9; H, 3.45; N, 16.5. $C_{10}H_9N_3S_2$ requires C, 47.8; H, 3.6; N, 16.75%). δ(^{1}H) 2.4 (3H, s), 6.45 (1H, br, CHOH), 6.85-7.0 (1H, m, H3'), 6.9 (1H, s, H5), 7.1-7.3 (2H, m, H2' and H4'). m/z 251 (M^+, 19%), 223 (M^+-N_2, 76%) 113 ($C_5H_5OS^+$, 60%), 111 ($C_5H_3OS^+$, 100%), 85 (48%).

Diphenyl(3-methyltriazolothiazol-6-yl)methanol (16). - Isolated in virtually quantitative yield and recrystallized from ether, the alcohol (16) had m.p. 144-146°C. (Found: C, 67.2; H, 4.4; N, 12.95. $C_{18}H_{15}N_3SO$ requires C, 67.3; H, 4.65; N, 13.1%). δ(^{1}H) 2.44 (3H, s), 5.31 (1H, br, OH), 6.38 (1H, s, H5), 7.32 (10H, s). δ(^{13}C) 10.78 (q), 78.56 (s, C(OH)), 118.16 (d, C5), 127.03 (d), 128.28 (d), 128.35 (d) (benzone ring carbons), 132.88 (s, C3), 134-78 (s, C3a), 137.17 (s, C6), 142.54 (s, Cl'). m/z 321 (M^+, 8%), 293 (M^+-N_2, 96%), 216 (43%), 163 (Ph_2C^+OH, 65%), 105 (100%), 77 ($C_6H_5^+$ 71%).

1-(3-Methyltriazolothiazol-6-yl)cyclohexanol (17). - Purified by Chromatotron (5:1) the cyclohexanol (17) crystallized from cyclohexane, m.p. 121-123°C (54%). (Found: C, 55.5; H, 6.2; N, 17.75. $C_{11}H_{15}N_3S$ requires C, 55.7; H, 6.3; N, 17.7%). δ(^{1}H) 1.3-2.2 (10H, m), 2.48 (3H, s), 3.75 (1H, br, OH), 6.9 (1H, s, H5). δ(^{13}C) 10.85 (q), 21.85 (t, C3' and C5'), 25.38 (t, C4'), 35.21 (t, C2' and C6'), 71.23 (s, Cl'), 112.58 (d, C5), 132.6 (s, C3), 135.03 (s, C3a), 140.05 (s, C6). m/z$^+$

237 (M^+), 209 (M^+-N_2, 100%), 166 (97%), 155 (32%), 138 (33%), 111 (85%), 99 (30%), 81 (55%, $C_6H_{11}^+$).

3.6-Dimethyltriazolothiazole (18). - Purified by Chromatotron (5:1) as a solid of indeterminate melting point, compound (18) was characterized by its spectra. $\delta(^1H)$ 2.35 (3H, s), 2.5 (3H, brs), 6.6 (1H, brs, H5). m/z 153 (M^+, 27%), 125 (M^+-N_2, 89%), 85 (32%) 82 (89%), 72 $CH_3CH{=}C{=}S^+$).

3-Phenyl-6-trimethylsilyltriazolothiazole (19). - Obtained as a solid from cyclohexane, m.p. 163-164°C (cyclohexane) in 44% yield and characterized by spectra. $\delta(^1H)$ 0.05 (9H, s), 7.3-7.6 (4H, m, 3ArH + H5), 7.75-7.9 (2H, d, H2' and H6'). m/z 245 (small, M^+-N_2), 174 (14%), 173 (M^+-N_2 C_3H_8Si, 100%).

4-Methoxyphenyl(3-phenyltriazolothiazol-6-yl)methanol (20). - Purified by Chromatotron and recrystallized from ethyl acetate (64% yield) the alcohol (21) had m.p. 161-162°C (Found: C, 63.9; H, 4.45; N, 12.3. $C_{18}H_{15}N_3O_2S$ requires C, 64.1; H, 4.45; N, 12.45%). $\delta(^1H)$ 3.65 (3H, s), 4.5 (1H, br, OH), 6.75 (2H, d), 6.85 (1H, s, CHOH), 7.2 (5H, m), 7.25 (1H, s, H5), 7.6-7.75 (2H, m).

2-Thienyl(3-phenyltriazolothiazol-6-ylmethanol (21). Purified by Chromatotron, the alcohol (21) was obtained as a solid m.p. 139-143° (cyclohexane). Analyses were inconsistent. $\delta(^1H)$ 6.85 (1H, s, CH), 6.9 (2H, m, H5 and H3'), 7.15 (5H, bs, C_6H_5), 7.3 (2H, m, H2',H4'). m/z 285 (M^+-N_2, 2%), 174 (13%), 173 (100%, *characteristic of all 3-phenyltriazolothiazoles*), 147 (24%), 121 (35%).

1-(3-Phenyltriazolothiazol-6-yl)cyclohexan-1-ol (22). - Purified by Chromatotron (5:1) and crystallized from cyclohexane, the cyclohexanol (22) had m.p. 165-167°C (85% yield). (Found: C, 63.95; H, 5.4; N, 14.0. $C_{16}H_{17}N_3SO$ requires C, 64.2; H, 5.35; N, 14.05%). $\delta(^1H)$ 1.36-2.24 (10H, m), 3.65 (1H, br, OH), 7.0 (1H, s, H5), 7.35 (1H, m, H4') 7.48 (2H, t, H3', H5'), 7.84 (2H, dd, J=8 and 1.95 Hz, H2' and H6'). m/z 299 (M^+, 4.5%), 271 (M^+-N_2, 100%), 155 (76%).

Ring Opening to Give 2,4-Disubstituted Thiazoles. The general procedures have been given in the preceding paper.[1] Most samples were characterized by n.m.r. spectroscopy, but one in each series was completely characterized, either by microanalysis and spectra, or as single pure peaks on a Hewlett-Packard GC5890 linked to Mass Selective Detector Model 5970B controlled by HP59970C Chemstation.

2-(1,1-Dibromoethyl)-4-trimethylsilylthiazole (24). Isolated in 70% yield and purified by bulb distillation, the thiazole (24) had b.p. 120°C/0.08 mm Hg. (Found: C, 27.5; H, 3.65; N, 4.0. $C_8H_{13}Br_2NS$ requires C, 28.0; H, 3.8; N, 4.1%). $\delta(^1H)$ 0.2 (9H, s), 2.9 (3H, s), 7.4 (1H, s, H5). m/z 344, 342, 340 (M^+-1 isotopes), 264, 262 M^+-Br isotopes), 248, 246, 139, 137.

1-(4-Trimethylsilylthiazol-2-yl)ethanol (25). - Recrystallized from petrol (b.p. 40-60°C) the thiazolylethanol (25) (54% yield) had m.p. 100.5-102°C and showed a single peak on gc/ms of m/z 201, 186, 170, 168, 158, 115, 75, 73, 45,

43. δ(^{1}H) 0.2 (9H, s), 1.45-1.5 (3H, d, J=6 Hz), 4.1-4.5 (1H, br, OH), 4.95-5.25 (1H, q, J=6 Hz), 7.3 (1H, s, H5).

2-Acetoxymethyl-4-(1-hydroxycyclohexan-1-yl)thiazole (33). - Obtained as one component by separation on a Chromatotron of the mixed acetates obtained when the mixed triazolothiazoles (8) and (9) were boiled with glacial acetic acid. The alcohol (33) had m/z 235 (50%, M-18), 195 (28%), 194 (30%), 177 (82%), 176 (32%), 149 (58%), 136 (31%), 43 (100%). δ(^{1}H) 1.4-1.95 (4H, m), 2.0-2.6 (6H, m), 2.15 (3H, s), 5.35 (2H, s), 6.55-6.9 (1H, brs) 7.0 (1H, s, H5). Distillation caused dehydration to give the cyclohexene (34), b.p. 110-120°C/0.05 mm Hg (bulb tube). (Found: C, 60.75; H, 6.2; N, 5.9. $C_{12}H_{15}NSO_2$ requires C, 60.75; H, 6.35; N, 5.9%). δ(^{1}H) 1.6-1.8 (4H, m), 2.15 (3H, s), 2.2-2.4 (4H, m), 5.35 (2H, s), 6.74-6.77 (1H, m, CH=), 6.98 (1H, s, H5).

(2-Acetylthiazol-4-yl)-2-thienylmethanone (37). - Oxidation of the alcohol (15) with selenium dioxide in boiling dioxan, followed by purification using the Chromatotron (5:1) and recrystallization from ether gave the diketone (37), m.p. 131-132°C (after sublimation) in 63% yield. (Found: C, 49.85; H, 2.85; N, 5.8. $C_{10}H_7NS_2O_2$ requires C, 50.65; H, 2.95; N, 5.9). The compound gave a single peak on g.c. with M^+ 237 (Calc. 237). δ(^{1}H) 2.7 (3H, s), 7.0-7.15 (1H, m, H4'), 7.6-7.7 (1H, brd, H5', J=6 Hz), 8.35-8.5 (1H, m, H3').

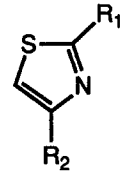
Spectral details of other thiazoles prepared are given in Table 3. All were purified but not subjected to microanalysis.

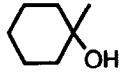
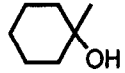
Acknowledgements. This work was carried out on a CASE studentship (to H.O.); the sponsors were Shell Synthetic Chemicals.

REFERENCES

1. Jones, G.; Ollivierre, H.; Fuller, L.S.; Young, J.M. preceding paper.
2. Metzger, J.V. Comprehensive Heterocyclic Chemistry, Vol. 6 p.254.
3. Gschwend, H.W; Rodriguez, H.R. Organic Reactions, 1979 **26**, 1.
4. Davies, J.S.; Jones, G. J. Chem. Soc. (c), 1970, 688.
5. Jones, G.; Sliskovic, D.R. J. Chem. Soc. Perkin Trans. 1, 1982, 967.
6. Mouat, D.J. Ph.D. thesis, University of Keele, 1989.

TABLE 3 Spectral Data for Thiazoles



			^{1}H Chemical Shifts (δ)		m/z		
Compound	R^1	R^2	H5	Other	M^+ Found	M^+ Req.	Base peak
26	$CH_3CH(OH)$	$CH(OH)C_6H_5$	6.8	1.45-1.55 (3H,d), 4.8-5.2 (1H,q), 5.8 (1H,s), 7.3(5H,s)	235	235	
27	$CH_3CH(OH)$	$CH(OH)C_6H_4OMe$-4	6.85	1.45-1.55 (3H,d), 3.7(3H,s), 4.8-5.15 (1H,q), 5.75 (1H, s), 6.75-6.9 (2H,d), 7.2-7.35 (2H,d)	265	265	43
28[a]	$C_6H_5CH(OH)$		6.75	1.4-1.8 (4H,m), 1.95-2.4 (6H,m), 4.1-4.5 (1H,br), 5.9 (1H,s), 6.4-6.7 (1H,br), 7.1-7.4 (5H,m)	289	289	77
30	$CH_3CH(OAc)$	$CH(OH)O_6H_4OMe$-4	6.85	1.55-1.65 (3H,d), 2.1 (3H,s), 3.7 (3H,s), 5.9-6.2 (1H,q), 6.7 (1H,s), 6.9-7.05 (2H,d), 7.2-7.35 (2H,d)	307	307	246
31	$CH_3CH(OAc)$	$C(OH)Ph_2$	6.6	1.5-1.6 (3H,d), 2.05 (3H,s), 4.0-4.3, (1H,br), 5.85-6.2 (1H,q), 7.2 (1OH,s)	353	353	105
35[b]	CH_3CO	$SiMe_3$	7.6	0.25 (9H,s), 2.6 (3H,s)	379[c]	379	110
36[d]	CH_3CO		7.45	1.4-2.1 (10H,m), 2.65 (3H,s), 3.8-4.5 (1H,br)	405[c]	405	387

[a] b.p. 94°/1 mm Hg [b] D.N.P had m.p. 179-182°C (ethanol) [c] Of the D.N.P. [d] D.N.P. had m.p. 247-249°C (methanol)