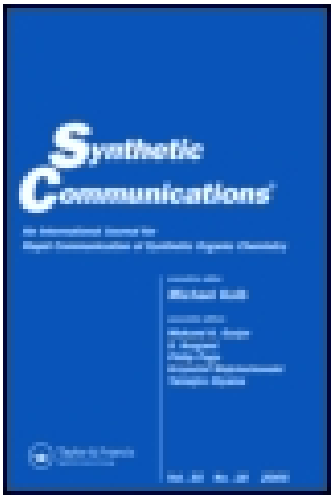

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4-Azidotetronic Acids: A New Class of Azido Derivatives

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4-AZIDOTETRONIC ACIDS:

A NEW CLASS OF AZIDO DERIVATIVES.

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Abstract: 4-Azidotetronic derivatives bearing different substituent groups on the carbon atom in position 3 were easily obtained by reaction of the corresponding 4-bromotetronic compounds with sodium azide in methanol at room temperature.

For several years our research group has dealt with a reactivity of 2-substituted arylazides as building blocks for synthesis of nitrogen heterocycles[1]. Our recent program directed toward the exploitation of useful azides prompted us to investigate the synthesis of 4-azido-3-substituted-2*(5H)*-furanones (tetronic acid derivatives). Such a substrate is a vinylogous carboxylic acid and is characteristic

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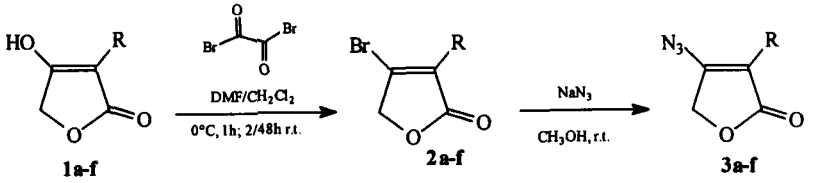


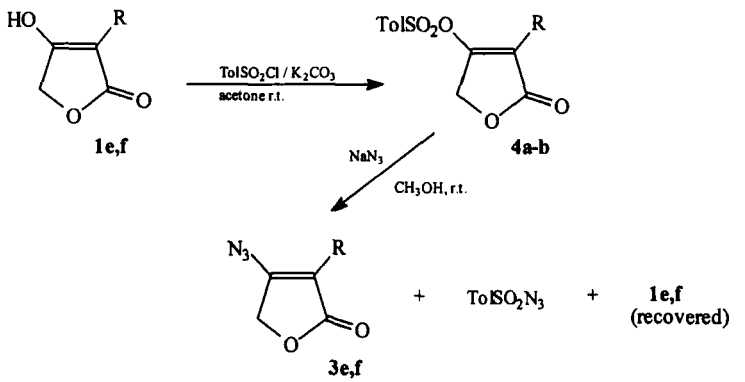
1,2,3 **R = a**: H; **b**: C_6H_5; **c**: 4-ClC_6H_4; **d**: 4-$H_3COC_6H_4$; **e**: CH_3; **f**: 3,4-$(H_3CO)_2C_6H_3$

Scheme 1

of a large number of sponges, fungal and lichen metabolites as well as compounds with antibiotic[2], anticoagulant[3] and insecticidal[4] activity. In recent years tetronic acid derivatives have received a renewed interest as useful cyclooxygenase[5], phospholipase[6] and HIV-1 protease inhibitors[7].

To our knowledge, 4-azidotetronic acids have not been described yet, and in general only occasional reports[8] exist for β-azido-vinyl-ketones and –esters. In the light of the biological signifiance of new tetronic acid derivatives, an interest exists in the preparation of synthons containing this moiety. We now describe an easy procedure for the preparation of azido derivatives. The reaction process is shown in the Scheme 1.

Tetronic acid derivatives **1**, which were obtained according to described methods[11,12], reacted with oxalyl bromide according to the method of Jas[9] for compound **2a**. Whilst a reaction time of 2h at room temperature was enough for **2a**, for the preparation of **2b-f** it was necessary to extend the reaction time as much as 48h; and for preparation of **2c, d, f,** it was also necessary to use an excess of oxalyl bromide to achieve complete transformation of reagents. All the



1,3 R = **e**: CH_3; **f**: 3,4-$(H_3CO)_2C_6H_3$ **4** R = **a**: CH_3; **b**: 3,4-$(H_3CO)_2C_6H_3$

Scheme 2

compounds, except **2d** and **2f** were obtained in good yield (49 % - 90 %). The structures were validated by spectral data which are collected in Experimental. The subsequent reaction of **2a-f** with excess NaN_3 in methanol at room temperature afforded azides **3a-e** in 52-90% yields. Azide **3f** was obtained in poor yield (37%) and despite long reaction times the starting bromide **2f** was recovered. The substitution of the hydroxy group of tetronic acid in to the corresponding azide through its transformation to the halo-derivative appears to be mandatory with respect to other routes. In early experiments we have found that reaction of NaN_3 on tetronic acid tosylates **4a,b** (see Scheme 2) affords the expected azides **3e,f** only in about 20% yield, the main reaction product being tosylazide and substituted tetronic acids. This fact is understandable on the basis of the good leaving ability of the conjugate base of tetronic acid [10], which in the reaction with NaN_3 acts in competition with tosylate.

In conclusion, we have found a simple and general method for the preparation of both 4-bromo and 4-azido derivatives of tetronic acid. The flexibility of the methodology should also be suitable for the synthesis of further 3-substituted tetronic acids, useful intermediates for compounds with interesting biological properties.

Experimental

Melting points (uncorrected) were determined by a Büchi 510 (capillary) apparatus or an Electrothermal 9100 apparatus. IR spectra were recorded with a JASCO IR Report 100 spectrophotometer (nujol or neat). NMR spectra were obtained with Bruker AC 200 and Varian Gemini 200 instruments at 200 MHz.: chemical shifts are expressed in ppm (δ) relative to TMS, *J* values are given in Hz for solutions in $CDCl_3$ unless otherwise indicated. Mass spectra were performed by an electron impact ionization tecnique at 70 eV on a Finnigan MD 800 GCMS spectrograph. Column chromatography was performed using silica gel 60/70-230 ASTM/Merck with eluant indicated and analytical TLC on silica gel pates with F-254 indicator.

Tetronic acid **1a** is commercially available, **1b-d**[11],**1e**[12], and **2a**[9]were prepared according to described method. Unknown **1f** was synthesized similarly to **1d**: synthesis and analytical data are reported below. All reagents were commercial products.

3-(3,4-Dimethoxy-phenyl)-4-Hydroxy-*5H*-furan-2-one (1f):

Homoveratric acid (27.5g, 140 mmol) was added to a solution of Na (3.25g, 140 mmol) in EtOH (240 mL) and mixture was stirred at r.t. in nitrogen atmosphere for 10 min. Ethyl bromoacetate (15.5 mL, 140 mmol) was added and the stirred mixture was heated under reflux for 4 h. The ethanolic solution was concentrated and ether was added to viscous residue. Addition of ether gave a precipitate of salt (NaBr). The salt was filtered off and ethereal solution evaporated to dryness *in vacuo* yielded crude (3,4-dimethoxy-phenyl)-acetic acid ethoxycarbonylmethyl ester as an oil; yield: 23.7g, (60%):

^{1}H NMR: 1.26 (t, J= 7.0, 3H, CH_2CH_3), 3.69 (s, 2H, 3,4-$(H_3CO)_2C_6H_3CH_2$), 3.87 and 3.89 (2 s, 3H and 3H, OCH_3), 4.21 (q, J= 7.0, 2H, CH_2CH_3), 4.62 (s, 2H, CH_2O), 6.80-6.88 (m, 3H, 3,4-$(H_3CO)_2C_6H_3$).

The oil previously obtained (20g, 71 mmol) was added to a solution of *t*.BuOK (8g, 71 mmol) in *t*.BuOH (35 mL) and the mixture was stirred to reflux for 90 min. Water (70 mL) was added and the solution was extracted with ether (3 x 50 mL). The aqueous phase was acidified with HCl (2N) to give a orange precipitate recrystallized from EtOH; yield 14.2g (85%); mp 208-209°C. IR (nujol cm^{-1}): 1695 (C=O), 1620 (C=C), ^{1}H NMR: (DMSO-d_6): 3.75 and 3.76 (2 s, 3H and 3H, OCH_3), 4.75 (s, 2H, CH_2O), 6.95-7.00 and 7.47-7.60 (2m, 3H, Ph-H).

Anal. Calcd. for $C_{12}H_{12}O_5$: C, 61.01; H, 5.12. Found C, 61.38; H, 5.27.

4-Bromo-2*(5H)*-furanones 2b-f; General Procedure:

Bromination of **1a** according known method[9] gives 4-bromo derivative **2a**.

2a: Yield 78 %; mp: 77°C (Et_2O) (lit[9] 77°C); IR (nujol cm^{-1}): 1760,1725,1580; ^1H NMR: 4.87 (d, *J*=1.9, 2H, CH_2), 6.36 (t, *J*=1.9, 1H,vinylic H); MS, *m/z*= 164 (M^+, 75), 162 (M^+,78), 135 (M^+-HCO, 79), 133 (M^+-HCO, 85), 106 (M^+-CO_2, 66), 104 (M^+-CO_2, 65), 83 (M^+- Br, 100)

Anal. Calcd. for $C_4H_3BrO_2$: C, 29,47; H, 1.85. Found C, 29.71; H, 1.97.

Compounds **2b-f** were obtained by a modified procedure described below:

Method A: A suspension of **1b** or **1e** (30mmol) in anhydrous CH_2Cl_2 (2,2mL/1g starting matherial) was mixed , under nitrogen, to DMF (39mmol). Checking strictly the inner temperature (0°C, ice-salt bath) 36 mmol of oxalyl bromide were dropped in about 1h. Stirring was kept for 2h at 0°C, then the mixture was left standing at r.t. (**1b** for 19 h ; **1e** for 4h.). The mixture was poured into H_2O. The aqueous layer was extracted with ether (3 x 50 mL) The combined organic extracts washed with $NaHCO_3$ solution, NaCl solution and dried on Na_2SO_4 were evaporated to dryness. The oily residue by trituration with ether furnished **2b** as orange and **2e**[13]as cream crystals respectively.

2b: Yield 90%; mp: 65°C (Et_2O); IR (nujol, cm^{-1}): 1740, 1660; ^1H NMR: 4.95 (s, 2H, CH_2), 7.35-7.85 (m, 5H, Ph-H); MS, *m/z*= 240 (M^+, 25), 238 (M^+, 25), 159 (M^+-Br, 61), 131 (M^+-Br-CO, 26), 115 (M^+-Br-CO_2,51), 103 (M^+ -Br-CO -CO 100)

Anal. Calcd. for $C_{10}H_7BrO_2$: C, 50.23; H, 2.95. Found C, 50.35; H, 3.13.

2e: Yield 49%; mp: 56°C (Et_2O) (lit[13]: 56-57 °C); IR (nujol cm^{-1}): 1765, 1660; ^1H NMR: 1.92 (t, *J*=2.44, 3H, CH_3), 4.78 (q, *J*=2.44, 2H, CH_2); MS, *m/z*=178 (M^+ 79), 176 (M^+ 87), 149 (M^+-HCO, 61), 147 (M^+-HCO, 60), 121 (65), 119 (70), 97 (M^+ -Br, 100), 81 (M^+-$C_5H_5O_2$, 21), 79 (M^+-$C_5H_5O_2$, 23), 69 (69), 67 (65) ,53 (74)
Anal. Calcd. for $C_5H_5BrO_2$: C, 33.92; H, 2.84. Found C, 34.13; H, 2.93.

Method B: The bromination was carried out using for **2c** anhydrous CH_2Cl_2 (4mL/ 1g starting **1c**) and 60 mmol of oxalyl bromide. For **2d** and **2f** anhydrous CH_2Cl_2 was used in the same ratio, but 90 mmol of oxalyl bromide and 48 h at r.t were necessary to complete conversion of corresponding 4-hydroxy-2*(5H)*furanones **1c, 1d, 1f**. 4-Bromoderivatives obtained as brown solid residue were purified by chromatography on a short silica gel column (ethyl acetate /cyclohexane 1: 8 as eluent) to give orange crystals of **2c, 2d, 2f**.

2c: Yield 72%; mp: 112°C,; IR (nujol cm^{-1}): 1740, 1625; ^1H NMR: 4.94 (s, 2H CH_2), 7.44 and 7.75 (d and d *J*= 8.8, 4H, aromatic AB-system); MS, *m/z*= 276 (M^+, 20), 274 (M^+, 78), 272 (M^+, 66), 195 (M^+ -Br, 60), 193 (M^+ -Br, 99), 167 (M^+ -Br -CO, 32), 165 (M^+ -Br -CO, 89), 151 (M^+ -Br -CO_2, 33), 149 (M^+ -Br -CO_2, 91), 139 (M^+ -Br -CO -CO, 70), 137 (M^+ -Br -CO -CO, 100), 136 (M^+ -HBr -CO -CO, 74), 114 (59), 113 (40), 102 (M^+ -Br -CO -CO -Cl, 60), 101 (M^+ -Br -CO -CO -HCl, 70), 99 (39), 75 (58), 74 (53), 63 (41), 62 (30), 51 (25)
Anal. Calcd. for $C_{10}H_6BrClO_2$: C, 43.91; H, 2.21. Found C, 44.16; H, 2.37.

2d: Yield 35%; mp: 102°C; IR (nujol cm^{-1}): 1740, 1580; ^1H NMR: 3.85 (s, 3H,

OCH_3), 4.91 (s, 2H, CH_2), 6.98 and 7.79 (d and d, *J*= 8.9, 4H, aromatic AB-system); MS, *m/z*= 270 (M^+, 71), 268 (M^+, 75), 189 (M^+, -Br, 84), 161(M^+ -Br -CO, 96), 145 (M^+ -Br –CO_2, 67), 133 (M^+ -Br -CO -CO, 100), 132 (M^+ -HBr -CO -CO, 40), 102 (75), 89 (39), 76 (30), 75 (26), 63 (31).

Anal. Calcd. for $C_{11}H_9BrO_3$: C, 49.09; H, 3.37. Found C, 49.31; H, 3.49.

2f: Yield 35%; mp: 135-136°C; IR (nujol cm^{-1}): 1750, 1620; ^1H NMR: 3.93 (s, 6H, OCH_3), 4.92 (s, 2H, CH_2), 6.93-6.98 and 7.39-7.50 (2 m,3H, Ph-H); MS, *m/z*= 300 (M^+ 75), 298 (M^+ 76), 219 (M^+ -Br, 44), 191(M^+ -Br -CO, 76), 176 (M^+ -Br –CO_2, 27), 163 (M^+ -Br -CO -CO, 100), 148 (35), 147 (34), 132 (24), 131 (40), 102 (24), 89 (31), 63 (28).

Anal. Calcd. for $C_{12}H_{11}BrO_4$: C, 48.18; H, 3.70. Found C, 47.96; H, 3.53.

4-Azido-3-substituted-furan-2*(5H)*-ones 3a-f: General Procedure

To a solution of **2a-f** (20 mmol) in methanol (50mL) protected from light was added NaN_3 (50mmol) at r.t. The reaction mixture was stirred and checked by TLC (eluent ethyl acetate/cyclohexane: 3/2) until disappearance of the starting 3-bromo-furan-2(5H)-ones for the time indicated next to each compound. The solvent was evaporated at reduced pressure and the solid residue treated with benzene (100mL). From the suspension obtained was filtered off the NaN_3 excess and the benzene solution washed with water. The organic layer was dried (Na_2SO_4) and then evaporated in vacuum at 25°C to leave a raw material. Azide **3b** crystallized from benzene. Chromatography with silica gel (eluent ethyl

acetate/cyclohexane: 3/7) of crude compounds yielded as crystal or oil the pure azides **3a,c-f**.

3a React. time: 3 h; yield 90%; oil; IR (nujol cm^{-1}): 2100, 1760,1730; ^1H NMR: 4.60 (d, *J*=1.50, 2H, CH_2), 5.60 (d, *J*=1.50, 1H, vinylic H); MS, *m/z*= 86 (M^+-CH -CN, 57), 68 (M^+ -N_2 -HCO, 100), 45 (37), 43 (27), 42 (28), 41 (52), 40 (M^+ -N_2 -CO -HCO, 85), 39 (M^+ -N_2 -CO -H_2CO, 23).

Anal. Calcd. for $C_4H_3N_3O_2$: C, 38.40; H, 2.42; N, 33.59. Found C,38.57; H, 2.49; N, 33.31.

3b React. time: 21 h; yield 84%; 110°C. dec.; IR (nujol cm^{-1}): 2100, 1735,1660; ^1H NMR: 4.91 (s, 2H, CH_2), 7.30-7.50 (m, 3H, Ph-H), 7.75-7.90 (m, 2H, Ph-H); MS, *m/z*= 173 (M^+ -N_2, 88), 145 (M^+- N_2 -CO, 23), 144 (M^+- N_2 -HCO, 100), 117 (M^+- N_2 -CO -CO, 41), 116 (M^+- N_2 -CO -HCO, 52), 115(M^+- N_2 -CO -H_2CO, 22), 89 (73), 88 (30), 76 (33), 75 (26), 63 (62), 62 (48).

Anal. Calcd. for $C_{10}H_7N_3O_2$: C, 59.70; H, 3.50; N, 20.88. Found C, 59.89; H, 3.54; N, 20.54.

3c React. time: 24 h; yield 52 %; 92°C. dec.; IR (nujol cm^{-1}): 2090, 1735, 1620; ^1H NMR: 4.94 (s, 2H, CH_2), 7.39 and 7.83 (d and d, *J*=8.7, 4H, aromatic AB system); MS, *m/z*= 207 (M^+ -N_2, 76), 180 (M^+- N_2 -HCN, 33), 178 (M^+-N_2 -HCO, 100), 151 (M^+- N_2 -CO -CO, 35), 150 (M^+- N_2 -CO -HCO, 39), 123 (M^+- N_2 -CO - H_2CO -CN, 47), 114 (M^+- N_2 -H_2CO -CO -Cl, 41), 89 (33), 88(28), 87

(66), 86 (46) ,85 (27), 76 (46), 75 (70), 74 (58), 73 (41), 63 (67), 62 (69).

Anal. Calcd. for $C_{10}H_6ClN_3O_2$: C, 50.97; H, 2.56; N, 17.83. Found C, 51.28; H, 2.66; N, 17.51

3d React. time: 24 h; yield 63%; 87°C. dec.; IR (nujol cm^{-1}): 2090, 1750, 1615; ^1H NMR: 3.84 (s, 3H, OCH_3), 4.90 (s, 2H, CH_2), 6.95 and 7.80 (d and d, *J*=9.0, 4H, aromatic AB system); MS, *m/z*= 203 (M^+ -N_2, 100), 188 (M^+ -N_2,-CH_3, 7)174 (M^+ -N_2, -HCO, 86), 159 (M^+ -N_2, -CO_2, 58), 146 (24), 132 (M^+ -N_2, -CO_2 - HCN,36), 131 (M^+ -N_2 -CH_3 -CO -H_2CO, 31), 119 (M^+- N_2 -CO -H_2CO -CN, 23), 116 (30), 104 (25), 103 (31), 89 (46), 77 (36), 76 (68)75 (61), 74 (49), 63 (74), 62 (41).

Anal. Calcd. for $C_{11}H_9N_3O_3$: C, 57.14; H, 3.92; N, 18.17. Found C, 57.17; H, 4.05; N, 17.85.

3e React. time: 5h; yield 70%; oil; IR (nujol cm^{-1}): 2090, 1740, 1650; ^1H NMR: 1.84 (t, *J*=1.75, 3H, CH_3), 4.70 (q, *J*=1.75, 2H, CH_2); MS, *m/z*= 82 (M^+ -N_2 -HCO, 87), 55 (M^+ -N_2 -HCO -HCN, 96), 54 (M^+ -N_2 -HCO -CO,100), 32 (32).

Anal. Calcd. for $C_5H_5N_3O_2$: C, 43.16; H, 3.62; N, 30.20. Found C, 43.47; H, 3.51; N, 29.88.

3f React. time: 48h; yield 37%; 130-132°C. dec. IR (nujol cm^{-1}): 2090, 1720, 1630; ^1H NMR: 3.92 (s, 6H, OCH_3), 4.91 (s, 2H, CH_2), 6.89-6.94 and 7.44-7.49 (2m, 3H, Ph-H); MS, *m/z*= 233 (M^+ -N_2, 54), 218 (M^+ -CH_3, 32), 204 (M^+ -N_3 -

CH_3, 12), 174 (M^+ -N_3 -CH_3, -H_2CO, 10), 172 (13), 146 (M^+ -N_3 -CH_3, -H_2CO, -CO, 100), 89 (16), 77 (21), 76 (45), 75 (26), 63 (44), 62 (25).

Anal. Calcd. for $C_{12}H_{11}N_3O_4$: C, 55.17; H, 4.24; N, 16.08. Found C, 55.35; H, 4.33; N, 15.75.

4-Toluensulfonate-3-substituted 2*(5H)*-furanones 4a-b: General Method

4-Hydroxyfuran-2 *(5H)*-one **1e** or **1f** (40 mmol) respectively was added to a mixture of 4-toluensulfonylchloride (48 mmol) and potassium carbonate (96 mmol) in acetone (70 mL). The mixture was stirred at r.t. overnight, filtered and the filtrate evaporated to dryness under reduced pressure . The crude residue was dissolved in ether and the remaining inorganic precipitate was filtered off. The ethereal solution was evaporated and white solid crystallized from solvent shown below.

4a: Yield 70%; mp: 70-71°C (Et_2O); IR (nujol cm^{-1}): 1750, 1690; ^1H NMR: 1.56 (t, *J*=1.9, 3H, CH_3 C-3), 2.49 (s, 3H, CH_3), 4.82 (q, *J*=1.9, 2H, CH_2), 7.42 and 7.84 (d and d, *J*=8.1, 4H, aromatic AB system); MS, *m/z*= 268 (M^+, 3), 155 (M^+ -$TolSO_2$, 97), 91 (100), 65 (79).

Anal. Calcd. for $C_{12}H_{12}O_5S$: C, 53.72; H, 4.51. Found C, 53.50; H, 4.37.

4b: Yield 61%; mp: 133°C (CH_2Cl_2); IR (nujol cm^{-1}): 1730, 1630; ^1H NMR: 2.43 (s, 3H, CH_3), 3.79 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 5.06 (s, 2H, CH_2), 7.19-7.39 (m, 3H, Ph-H dimethoxysubstituted), 6.81 and 7.77 (d and d, *J*=8.5, 4H, aromatic AB system); MS, *m/z*= 235 (M^+ -$TolSO_2$, 100), 177 (M^+ -$TolSO_2$ -

H_2CO, -CO, 64), 163 (22), 162 (31), 149 (36), 147 (25), 119 (379, 91 (67), 89 (36), 76 (47), 75 (49), 63 (50).

Anal. Calcd. for $C_{19}H_{18}O_7S$:C, 58.45; H, 4.64. Found C, 58.12; H, 4.49.

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