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THE CHEMISTRY OF FULMINIC ACID REVISED†

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Abstract—The availability of a new synthesis of fulminic acid by hydrolysis of trimethylsilanecarbonitrile oxide allowed a reinvestigation of the chemistry of the title compound. Thus, cycloadditions to olefinic and acetylenic dipolarophiles are improved with respect to previous results and the oligomerisation is proved to occur via the reactive species hydroxyiminoacetonitrile oxide **7** and hydroxyiminomethyl-hydroxyimino-acetonitrile oxide **8**. The Z-configuration, found for the oxime groups in these intermediates, is maintained in their derivatives, under kinetic control.

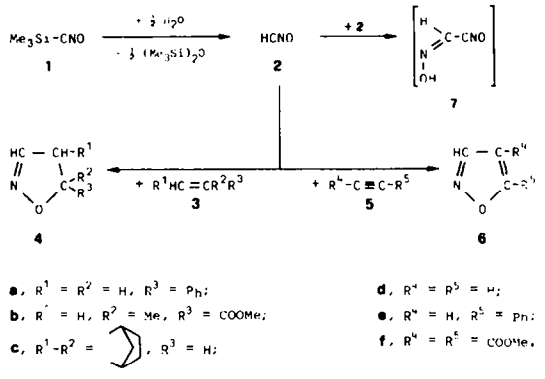
Quilico and Speroni first pointed out that some isoxazole derivatives can be generated by reaction of fulminic acid with acetylene derivatives.[1] The same authors later emphasised the role of nitrile oxides in the synthesis of isoxazole derivatives.[2] Since then, the cycloaddition of nitrile oxides to unsaturated compounds has become one of the most convenient routes to several heterocycles:[3] thus, fulminic acid (to be regarded as the simplest term, formonitrile oxide) leads to isoxazole derivatives without substituents in the 3-position. This method has been successfully employed by Huisgen and Christl, who generated the dipole **2** from a convenient precursor, formohydroxamoyl iodide.[4] However either this precursor and the one employed previously (sodium fulminate) appear now to be superseded by trimethylsilanecarbonitrile oxide **1**, a material easy to prepare and remarkably stable,[5] which on hydrolysis in organic solvents immediately generates fulminic acid.[6]

1:1 *Cycloadditions*

The dipole **2** was generated *in situ* by slowly adding a solution of **1** in anhydrous THF to a solution of the dipolarophile **3** or **5** and water in THF: the expected cycloadducts **4** or **6** (Scheme 1) were obtained in good yields even with no excess of dipolarophile. The results are summarized in the table of ref. 6. By this procedure, the dimerisation of fulminic acid **2** to **7** was largely reduced and only with the less reactive dipolarophiles (**5d**, **5e**) minor amounts of the 2:1 adducts were found. Such 2:1 adducts have been known for a long time to arise from fulminic acid and considered as an indirect evidence of the reactive dimer **7**.[4]

The regioselectivity in the 1:1 addition has been discussed previously, as well as the *exo* approach observed in the cycloaddition to norbornene **3c**. The last ascription rests on the very low coupling constants between each bridgehead proton and the adjacent isoxazoline H-atoms.

The technique reported here is particularly recommended for the preparation of deuteriated fulminic acid and of 3-deuteroisoxazole derivatives therefrom, as illustrated by the synthesis of the adduct **4c**–d_1.



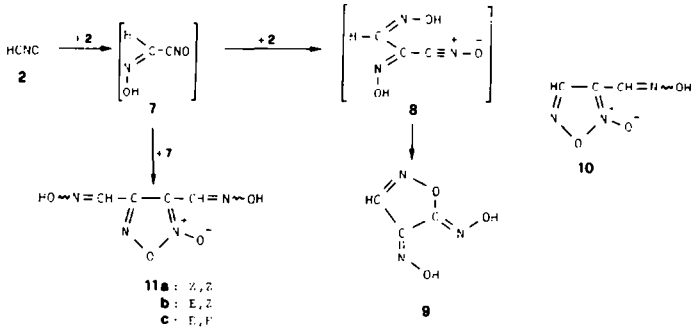
Scheme 1.

Polymerisation

References to the wide earlier literature concerning the polymerisation of fulminic acid can be found in ref. 3 (pp. 69–75), where the subject was reviewed. The main product of the spontaneous exothermic polymerisation in solution is a trimer ("metafulminuric acid", m.p. 85–86°, dec.),[7] whose structure was established[7] as 4,5-dihydro-4,5-bis(hydroxyimino)isoxazole **9**. Other oligomers, isolated as minor by-products, are: a tetramer ("α-isocyanilic acid", m.p. 170–172°, dec.)[8] identified as 3,4 - bis(hydroxyiminomethyl) - 1,2,5 - oxadiazole 2-oxide[8] (*E,E* configuration, **11c**)[9] and another trimer, m.p. 152°,[10] identified[11] with a material formerly described as nitrocyanacetaldoxime[12] (α-isomer).[13] The structure of 3 - (hydroxyiminomethyl) - 1,2,5 - oxadiazole 2-oxide **10** was assigned to this trimer, on spectral (IR, MS) and chemical grounds.[11]

As early as in 1925, Wieland postulated the illustrated formation mechanism for the oligomers **9** and **11** via the unstable intermediates **7** and **8**[8] (Scheme 2). This view is fully confirmed by our ^{1}H-NMR observations on a 2 M solution of fulminic acid in THF: the unstable intermediates **7** and **8** are detected during a short period, their signals being gradually replaced by those of metafulminuric acid **9** and of the tetramers **11** (Experimental). In addition, a sharp singlet at δ 8.75 and two equivalent broad singlets at δ 7.40 and 8.40 are detected: however, these signals cannot be ascribed to the trimer **10**, as either the α- or the β-isomer, prepared as reported,[11] exhibit different spectra.

† Dedicated to the memory of Professor Giovanni Speroni who died on 14 March 1984.



Scheme 2.

The reactive intermediates **7** and **8** have been trapped by cycloaddition, as reported in the next section: not only was their identity thus confirmed, but their configurations established, too. The dimer **7** is produced as *Z*-oxime, therefore we expect this configuration to be maintained, under kinetic control, in the tetramer **11a**. Conversion of this tetramer into the thermodynamic isomer **11c**, with *E,E* configuration, occurs via the intermediate **11b** isomer. The ^{13}C-NMR signals of the isomers **11b** and **11c** are identified on the basis of previous assignments of furoxan derivatives.[14,15] A comparison of their chemical shifts shows that the C—CH pair apart from the N-oxide group does not change significantly, whereas the other pair does, thus indicating that the configuration is opposite in the hydroxyiminomethyl group adjacent to the N-oxide, i.e. *Z* in **11b**, *E* in **11c**.

In the unstable trimer **8**, both oxime groups are in the *Z* configuration, as shown in the next section: the stereochemistry is therefore suitable for intramolecular cyclisation, which indeed occurs very rapidly.

The observed stereochemistry of the polymerisation of fulminic acid is reminiscent of the analogous results reported for the nucleophilic attack to nitrile oxides.[16,17]

Oligomers cycloaddition; 2:1 *and* 3:1 *adducts*

Further insight into the polymerisation mechanism and the structure of the intermediates **7** and **8** has been obtained by adding an excess of a strong dipolarophile (namely norbornene **3c**) to the solution during the polymerisation process: quenching of the reactive species (those containing a CNO group), i.e. **2**, **7** and **8**, at different times was thus achieved by converting them into the corresponding cycloadducts **4c**, **12** and **16** respectively (Scheme 3).

At *ca* 30°, the monomer **2** is no longer detected (as **4c**, by ^{1}H-NMR) if the dipolarophile **3c** is added 5 min after the preparation of **2**; the cycloadducts **12** and **16** are detected, besides some metafulminuric acid **9**. These cycloadducts can be isolated but, if the solution is set aside at room temp, they convert into the thermodynamically more stable stereoisomers **13** and **17** in a few hours.

The actual configuration of the two isomeric oximes **12** and **13** has been established by treatment with 0.1 equiv. of aqueous NaOH at room temp: the stable oxime **13** is unaffected, whereas the oxime **12** is converted immediately into the isomeric substituted 1,2,5-oxadiazole **14**, according to a well-known heterocyclic rearrangement.[18,19] On prolonged treatment with the base (stoichiometric amount), the oxadiazole **14** undergoes ring-opening, re-cyclisation and hydrolysis to the lactone **15** (Scheme 3).

As to the conversion **16** → **17**, the considerable downfield shift of the H—C=N proton ($\Delta\delta$: 0.5) indicates an isomerisation *Z* → *E* analogous to that observed on the 2:1 adduct **12** ($\Delta\delta$: 0.6). The configuration of the adjacent ketoxime in the stable isomer **17** was established on the basis of its conversion into the aldoxime **18**: this heterocyclic rearrangement requires a *Z* configuration for the ketoxime group.[19] Thus, all oxime groups in the intermediates **7** and **8** are *Z*.

In all compounds **12** to **18** no appreciable coupling is observed between the bridgehead protons and those of the adjacent CH groups. As for the 1:1 adduct **4c**,[4] this finding is assumed as a proof of the *exo*-structure for these compounds.

EXPERIMENTAL

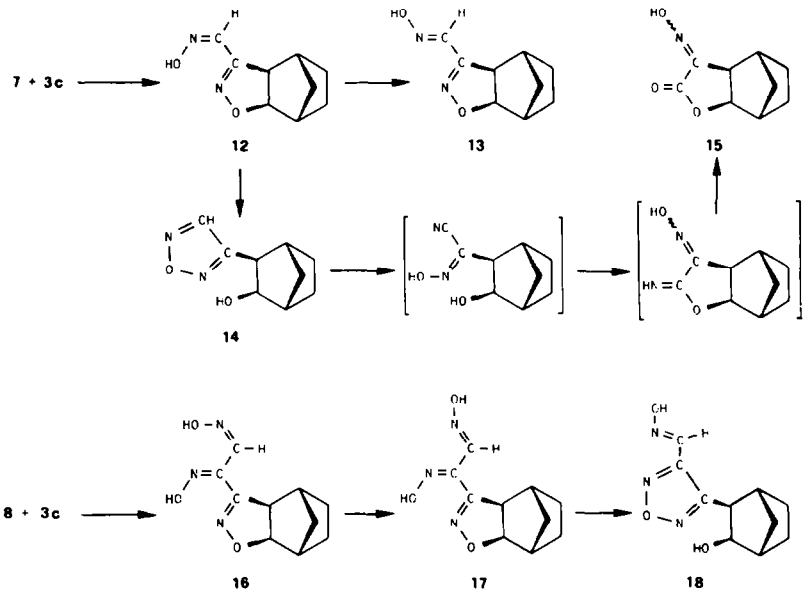
M.ps were observed with a microscope RCH Kofler apparatus. Vacuum distillations were carried out by a Büchi GKR-50 Kugelrohr distillator: the oven temp is reported. Chromatographic separations were performed under pressure, using the "flash-column" technique[20] (silica gel). IR spectra were recorded with a Perkin–Elmer 283 spectrophotometer, NMR spectra ($CDCl_3$ solutions, unless otherwise stated) with Perkin–Elmer R 32 (^{1}H, 90 MHz, CW) and Varian FT-80 A (^{13}C, 20 MHz) spectrometers: the chemical shifts are given in ppm from TMS; coupling constants J (in Hz) refer to $^3J_{HH}$ or to $^1J_{CH}$. Mass spectra were recorded at 70 eV by GC inlet on a 5790A–5970A Hewlett–Packard instrument, but for compound **18** by direct inlet on a Perkin–Elmer 270 mass spectrometer. Microanalyses were carried out with a Perkin–Elmer 240 C elemental analyser.

Trimethylsilanecarbonitrile oxide was prepared as previously reported.[5]

1:1 *Cycloadditions: isoxazolines* **4** *and isoxazoles* **6**

General procedure. A solution of trimethylsilanecarbonitrile oxide **1** (10 mmol), in anhydrous tetrahydrofuran (THF, 10 ml), was added dropwise to a stirred solution of dipolarophile (10 mmol) in THF containing 5% water (10 ml). The solution was then dried over Na_2SO_4, the solvent removed, and the product distilled.

5-Phenyl-4,5-dihydroisoxazole **4a**. Addition time: 3 hr at room temp; crude, 1.36 g (92%). B.p. 100°/0.07 mmHg, yield 1.12 g (76%). ^{1}H-NMR in agreement with the lit.;[4] ^{13}C-NMR: δ 145.3 d (J = 189), 140 s, 128.5 d, 127.9 d, 125.5 d, 79.6 d (J = 152), 43.4 t (J = 136); MS: *m/z* 147 (20%, M^+), 146 (12), 130



Scheme 3.

(7), 129 (15), 115 (15), 107 (20), 106 (45), 105 (68), 104 (100), 103 (21), 91 (20), 79 (25), 78 (55), 77 (89), 69 (25), 51 (66), 44 (51), 41 (38).

5 - *Carbomethoxy* - 5 - *methyl* - 4,5 - *dihydroisoxazole* **4b**. Addition time: 1 hr, reflux; crude, 1.27 g (89%). B.p. 70–80°/0.06 mmHg, yield 1.15 g (80%). IR (neat), cm^{-1} 1745 vs ($\nu_{C=O}$), 1610 m ($\nu_{C=N}$); ^{1}H-NMR: δ 7.13 s (1H), 3.72 s (3H), 3.62–2.73 AB system (J_{gem} = 18; δ_A 3.47, δ_B 2.89), 1.55 s (3H); ^{13}C-NMR: δ 171.8 s, 145.5 d (J = 190), 83.0 s, 52.3 q (J = 148), 45.0 t (J = 136), 22.6 q (J = 130); MS: *m/z* 143 (0.6%, M^+), 128 (0.2), 113 (0.2), 112 (0.2), 103 (1.2), 85 (4), 84 (63), 83 (10), 69 (3.5), 68 (3), 59 (6), 43 (100), 42 (35), 41 (10), 40 (3).

3a,4,5,6,7,7a - *Hexahydro* - 4,7 - *methanobenz*[d]*isoxazole* **4c** and **4c**–d_1. Addition time: 30 min at room temp; crude, 1.2 g (88%). B.p. 80–90°/0.1 mmHg, yield 0.94 g (68%). ^{1}H-NMR and IR in agreement with the lit.;[4] ^{13}C-NMR: δ 146.5 d, 84.1 d, 57.3 d, 41.9 d, 38.3 d, 31.6 t, 26.7 t, 22.6 t; MS: *m/z* 137 (45%, M^+), 120 (6), 110 (1), 109 (8), 107 (3), 106 (10), 83 (7), 82 (10), 80 (17), 79 (32), 77 (15), 70 (34), 68 (60), 67 (100), 53 (30), 43 (17), 41 (52).

The 3-deutero analogue, **4c**–d_1, was prepared similarly, but using D_2O instead of H_2O and an excess of dipolarophile **3c** (5 equiv.): yield 80%, with respect to **1**; isotopic purity, 90% (from ^{1}H-NMR), 85% (from MS). MS: *m/z* 138 (42%, M^+), 137 (6), 121 (8), 110 (6), 109 (12), 108 (4), 107 (6), 106 (2), 84 (6), 83 (5), 82 (15), 81 (33), 80 (18), 79 (25), 77 (10), 71 (32), 68 (67), 67 (100), 53 (29), 43 (11), 41 (49).

Isoxazole **6d**. A solution of trimethylsilanecarbonitrile oxide **1** (10 mmol) in anhydrous THF (10 ml) was added dropwise at room temp to a stirred solution of THF containing water 5% (50 ml), constantly saturated with acetylene **5d** (atm. pressure). When the addition was complete (1.5 hr), the adduct **6d** was prevalent, besides some 2:1 adduct derived from the dimer **7** (ratio 6:1, by ^{1}H-NMR). The solution was concentrated in part; powdered $CdCl_2 \cdot 2.5\ H_2O$ (4 g) was added and the mixture stirred for 20 hr. The precipitated complex salt was collected, washed with water and with THF, then dried *in vacuo* at room temp and decomposed at 150°/0.6 mmHg: a 1:1 mixture of isoxazole **6d** and THF was collected (28%).

5-*Phenylisoxazole* **6e**. A solution of trimethylsilanecarbonitrile oxide **1** (15 mmol) in anhydrous THF (10 ml) was added dropwise at room temp to a stirred solution of phenylacetylene **5e** (30 mmol) in THF containing water 10% (5 ml). After the addition was complete (1.5 hr), the solution was dried and concentrated, and the residue column chromatographed (silica gel, eluant CH_2Cl_2) to give the isoxazole **6e** (1.1 g, yield 50.6%), and the 2:1 *adduct* derived from **7** (0.31 g, yield 22%; m.p. 151°, from benzene; reported[21] m.p. 150–151°).

5-*Phenylisoxazole* **6e**. ^{1}H-NMR: δ 8.23 d (J = 3), 7.8–7.25 m, 6.42 d (J = 3); ^{13}C-NMR: δ 168.8 s, 150.3 dd (J = 186, $^2J_{CH}$ = 5.6), 129.7, 128.5, 126.8 and 125.3 (phenyl), 98.3 dd (J = 173, $^2J_{CH}$ = 9.4); MS: *m/z* 145 (61%, M^+), 105 (100), 77 (81), 51 (38), 50 (20), 43 (15), 39 (13).

3 - *Hydroxyiminomethyl* - 5 - *phenylisoxazole* (2:1 *adduct*). ^{1}H-NMR: δ 8.52 br s, 8.3 s, 7.2–7.9 m (phenyl), 6.8 s; ^{13}C-NMR: δ 170.4 s, 158.4 s, 141.5 d (J = 174), 130.4, 129.0, 126.8 and 125.8 (phenyl), 96.4 d (J = 187); MS: *m/z* 188 (28%, M^+), 172 (12), 170 (23), 161 (5), 145 (6), 116 (6), 105 (100), 77 (66), 51 (30), 50 (10), 45 (7), 40 (8).

4,5-*Dicarbomethoxyisoxazole* **6f**. Addition time: 30 min at room temp. By distillation, after a 0.1 g head at 60–80°/0.1 mmHg (starting ester **5f**), a fraction was collected at 90–100°/0.07 mmHg, containing the same ester (10%) and the adduct **6f** (90%): 1.41 g, neat yield 68%; ^{1}H-NMR: δ 8.65 s, 4.02 s, 3.91 s; ^{13}C-NMR: δ 160.1 s, 159.5 s, 156.3 s, 150.5 d (J = 194), 114.8 s, 53.2 q (J = 149), 52.4 q (J = 148); MS: *m/z* 185 (17.5%, M^+), 155 (15), 154 (96), 126 (36), 99 (10), 96 (9), 94 (21), 82 (32), 69 (23), 68 (23), 67 (19), 59 (100), 58 (30).

Polymerisation of fulminic acid

Trimethylsilanecarbonitrile oxide **1** (1.15 g, 10 mmol) was treated with ice-cold THF containing 5% water (5 ml), the solution temperature being initially maintained within 15°. The reaction was monitored by ^{1}H-NMR (6.5 to 9 δ in THF, probe temp): after 3 min, the main components were the *dimer* **7** (δ 6.72), the *trimer* **8** (δ 7.03), and *metafulminuric acid* **9** (δ 8.21); minor components were detected at δ 8.75 (unidentified), δ 7.40 and 8.40 (possibly another trimer) and at δ 7.24 and 7.49 (the kinetic tetramer **11a**). Later, the trimer **8** was converted completely (within 6 min at the probe temp) into **9**, which then evolved in a few hours; the dimer **7** afforded more slowly (completely in 3 to 4 hr) the mentioned tetramer **11a**, which was isomerised ($t_{1/2}$ *ca* 3 hr) to **11b** (δ 7.28 and 8.13) and this in turn to **11c** (δ 8.19 and 8.22, $t_{1/2}$ *ca* 1 d). The solution exhibited an IR absorption at 2280 cm^{-1}, gradually decreasing and ascribed to the dimer **7**.

After concentration, most metafulminuric acid **9** (insoluble in $CHCl_3$) was removed from the residue. Attempted separation of the minor products by column chromatography (eluant: $CHCl_3$–MeOH, 10:1) allowed only the stable

tetramer **11c** to be isolated, followed by a fraction containing a mixture of **11b** and **11c**.

3 - Z - *Hydroxyiminomethyl* - 4 - E - *hydroxyiminomethyl* - 1,2,5 - *oxadiazole* 2 - *oxide* **11b**. ^{13}C-NMR (DMSO-d_6): δ 151.3 s (C4), 138.4 d (CH-C4), 130.1 d (CH-C3), 106.9 s (C3).

3,4 - *Bis*(E - *hydroxyiminomethyl*) - 1,2,5 - *oxadiazole* 2 - *oxide* **11c**. M.p. 155–160° (dec.), identical with a sample of "α-isocyanilic acid", m.p. 160–161° (dec.) prepared as reported[9] (^{1}H-NMR and IR comparison); ^{13}C-NMR (DMSO-d_6): δ 150.5 s (C4), 138.4 d (CH-C4), 135.1 d (CH-C3), 109.0 s (C3).

The reported[11] stereoisomeric trimers 3-oxyiminomethyl-1,2,5-oxadiazole 2-oxides **10** (indicated as α and β) were prepared as described and found to be different from the polymer with ^{1}H-NMR signals at δ 7.40 and 8.40. ^{1}H-NMR (THF): α-isomer: δ 7.85 and 8.69; β-isomer: δ 7.33 and 9.06.

Kinetic adducts

3 - Z - *Oxyiminomethyl* - 3a,4,5,6,7,7a - *hexahydro* - 4,7 - *methanobenz*[d]*isoxazole* **12** *and* 3 - (1 - Z - *oxyimino* - 2 - Z - *oxyiminoethyl*) - 3a,4,5,6,7,7a - *hexahydro* - 4,7 - *methanobenz*[d]*isoxazole* **16**. Trimethylsilanecarbonitrile oxide **1** (1.91 g = 16.6 mmol), was dissolved in ice cold THF containing 5% water (8.3 ml) and the temp maintained at 15°. After 15 min, a 4 M solution of norbornene **3c** in THF was added (8.3 ml, 100% excess) and the mixture set aside for 15 min at 15°. On concentration *in vacuo* and flash-column chromatography of the residue (eluant: methylene chloride–acetone, 20:1), the adducts **12** (0.4 g, 27% yield), **16** (0.23 g, 19%) and **17** (0.28 g, 23%) were collected sequentially.

2:1 *Kinetic adduct* **12**. M.p. 92–102° (crude). IR (KBr), cm^{-1} 3240 s br (ν_{OH}), 1655 vw and 1550 ($\nu_{C=N}$); ^{1}H-NMR: δ 9.2 br s (OH), 7.45 s (H—C=N), 4.63 d (J = 6, HC—O), 3.57 d (J = 6, HC—C=N); ^{13}C-NMR: δ 152.8 s, 138.0 d, 89.2 d (HC—O), 57.6 d, 42.6 d, 40.2 d, 31.7 t, 27.3 t, 22.7 t; MS: *m/z* 180 (44%, M$^+$), 163 (10), 162 (5), 149 (8), 123 (30), 113 (25), 95 (18), 81 (71), 79 (31), 68 (37), 67 (100), 66 (25), 41 (51).

3:1 *Kinetic adduct* **16**. Colourless oil. IR, cm^{-1} 3240 s br (ν_{OH}), 1660 m and 1610 m ($\nu_{C=N}$); ^{1}H-NMR (Me_2CO-d_6): δ 11.47 br (two OH), 7.36 s (H—C=N), 4.62 d (J = 9, HC—O), 3.79 d (J = 9, HC—C=N); ^{13}C-NMR (Me_2CO-d_6): δ 151.9 s, 142.5 s, 139.7 d, 88.2 d (HC—O), 58.6 d, 42.6 d, 39.8 d, 32.0 t, 27.0 t, 22.7 t.

Thermodynamic adducts

3 - E - *Oxyiminomethyl* - 3a,4,5,6,7,7a - *hexahydro* - 4,7 - *methanobenz*[d]*isoxazole* **13** *and* 3 - (1 - Z - *oxyimino* - 2 - E - *oxyiminoethyl*) - 3a,4,5,6,7,7a - *hexahydro* - 4,7 - *methanobenz*[d]*isoxazole* **17**. The crude adducts mixture, obtained as above, was set aside at room temp for 1 day, then chromatographed to afford the adducts **13** (amount corresponding to 23.5% of the generated HCNO) and **17** (36%).

2:1 *Thermodynamic adduct* **13**. M.p. 159–161° (from CCl_4). (Found: C, 59.99; H, 6.68; N, 15.36. $C_9H_{12}N_2O_2$ (M = 180.21) requires: C, 59.99; H, 6.71; N, 15.55%.) IR (KBr), cm^{-1} 3200 s br (ν_{OH}), 1620 vw and 1580 m ($\nu_{C=N}$); ^{1}H-NMR: δ 9.1 br (OH), 8.05 s (H—C=N), 4.6 d (J = 9, HC—O), 3.28 d (J = 9, HC—C=N); ^{13}C-NMR: δ 154.7 s, 142.8 d, 88.8 d (HC—O), 55.25 d, 42.8 d, 38.9 d, 32.1 t, 27.1 t, 22.4 t; MS: *m/z* 180 (81%, M$^+$), 163 (14), 162 (10), 149 (10), 118 (10), 114 (21), 113 (59), 81 (22), 68 (50), 67 (100), 66 (27), 41 (40).

3:1 *Thermodynamic adduct* **17**. Evolves on attempted crystallisation; washed with $CHCl_3$, melts between 133 and 146°. (Found: C, 51.60; H, 5.77; N, 18.99. $C_{10}H_{13}N_3O_3$ (M = 223.23) requires: C, 53.81; H, 5.87; N, 18.82%.) IR (KBr), cm^{-1} 3240 s br (ν_{OH}), 1630 w br and 1550 w ($\nu_{C=N}$); ^{1}H-NMR (Me_2CO-d_6): δ 11.3 br (OH), 10.7 br (OH), 7.87 s (HC=N), 4.55 d (J = 8, HC—O), 3.6 d (J = 8, HC—C=N); ^{13}C-NMR (Me_2CO-d_6): δ 150.5 s, 146.8 d, 146.1 s, 87.0 d (CH—O), 58.95 d, 42.8 d, 39.0 d, 32.3 t, 26.9 t, 23.0 t; MS: *m/z* 223 (6%, M$^+$), 206 (24), 178 (100), 171 (19), 161 (21), 136 (21), 93 (28), 79 (46), 67 (90), 41 (66).

Rearrangement of the adduct **12**

3 - (1,2,5 - *Oxadiazol* - 3 - *yl*)*bicyclo*[2.2.1]*heptan* - 2 - *ol* **14**. A solution of KOH in EtOH (1 M, 0.1 equiv.) was added to an ice-cold solution of the adduct **12** in EtOH (0.5 M) and the mixture allowed to reach room temp. When **12** was no longer detected by ^{1}H-NMR (15 min) the solution was neutralised with ethanolic HCl (0.1 equiv.) and concentrated. The residue was dissolved in CH_2Cl_2, dried, concentrated and distilled: b.p. 150–165°/0.1 mmHg, yield 78%. (Found: C, 60.06; H, 7.05; N, 15.82. $C_9H_{12}N_2O_2$ (M = 180.21) requires: C, 59.99; H, 6.71; N, 15.55%.) IR (neat), cm^{-1} 3440 s br (ν_{OH}), 1565 m and 1560 sh ($\nu_{C=N}$); ^{1}H-NMR: δ 8.15 s, 4.07 d (J = 7), 3.17 d (J = 7); ^{13}C-NMR: δ 154 s, 142.1 d, 75.4 d, 44.1 d, 43.7 d, 40.6 d, 33.5 t, 28.6 t, 23.5 t; MS: *m/z* 180 (1%, M$^+$), 163 (14), 162 (10), 114 (21), 113 (59), 81 (22), 68 (50), 67 (100), 66 (27), 41 (40).

2 - *Oxo* - 3 - *oxyimino* - 4,7 - *methanoperhydrobenzo*[d]*furan* **15**. By treatment with 1 equiv. of ethanolic KOH, either compound **12** or **14** gave on acidification a mixture of products from which the lactone **15** was isolated (27% from **14**): m.p. 129°, from n-hexane + 5% $CHCl_3$. (Found: C, 60.33; H, 6.44; N, 7.97. $C_9H_{11}NO_3$ (M = 181.19) requires: C, 59.66; H, 6.12; N, 7.73%.) IR (KBr), cm^{-1} 3390 s br (ν_{OH}), 1740 vs ($\nu_{C=O}$), 1635 m ($\nu_{C=N}$); ^{1}H-NMR: δ 12.4 br, 4.69 d (J = 6), 2.98 d (J = 6); ^{13}C-NMR: δ 165.3 s, 146.0 s, 85.9 d, 45.8 d, 42.7 d, 40.7 d, 31.95 t, 27.2 t, 23.0 t; MS: *m/z* 181 (15%, M$^+$), 164 (19), 153 (7), 146 (10), 140 (21), 137 (15), 136 (16), 118 (72), 109 (36), 105 (31), 91 (61), 79 (77), 67 (100), 66 (74), 53 (43), 44 (12), 43 (11), 41 (75).

Rearrangement of the adduct **17**

3 - (4 - E - *Oxyiminomethyl* - 1,2,5 - *oxadiazol* - 3 - *yl*)*bicyclo*[2.2.1]*heptan* - 2 - *ol* **18**. By the same procedure described for the adduct **12**, the rearrangement of **17** was complete in 1.5 hr. The residue obtained on CH_2Cl_2 removal was column chromatographed (eluant: CH_2Cl_2–acetone, 10:1) to give **18**, m.p. 154–155°, yield 67%. A sample for analysis was recrystallised from $CHCl_3$–acetone (10:1), m.p. 160–161°. (Found: C, 54.03; H, 5.94; N, 18.65. $C_{10}H_{13}N_3O_3$ (M = 223.23) requires: C, 53.81; H, 5.87; N, 18.82%.) IR (KBr), cm^{-1} 3390 s br and 3300 s br (ν_{OH}), 1640 w br and 1560 w ($\nu_{C=N}$); ^{1}H-NMR (Me_2CO-d_6): δ 11.23 s (N—OH), 8.33 s (HC=N), 4.18 m (HC—O, becomes d, J = 7, when the alcoholic OH exchanges faster, on H_2O addition), 3.72 d (J = 5, C—OH, becomes s), 3.27 dd (J = 7, J = 2); ^{13}C-NMR (Me_2CO-d_6): δ 153.9 s, 150.1 s, 138.5 d, 75.3 d, 46.3 d, 45.0 d, 39.4 d, 34.1 t, 25.5 t, 24.2 t; MS: *m/z* 223 (8%, M$^+$), 206 (10), 178 (28), 170 (13), 160 (11), 119 (21), 118 (25), 105 (20), 93 (29), 81 (35), 79 (38), 67 (100), 57 (36), 53 (31), 43 (72), 41 (78).

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