A 1,2,3-Thiadiazole–1,2,3-Thiadiazole Rearrangement

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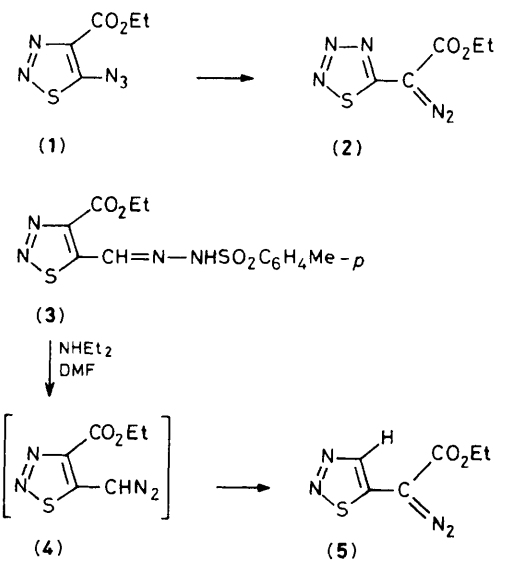
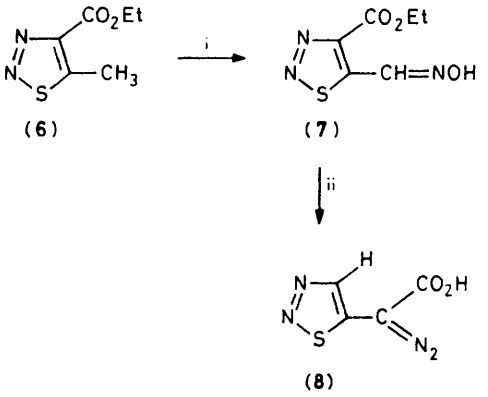
During its preparation, 4-ethoxycarbonyl-5-diazomethyl-1,2,3-thiadiazole (**4**) undergoes a ring transformation into the isomeric structure (**5**), but when the ester function in (**4**) is replaced by a phenyl group, no isomerization is observed.

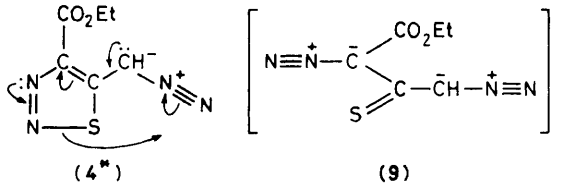
Recently, we reported a novel type of bond-switch rearrangement involving sulphur as the pivot atom: namely the transformation of a 5-azido-1,2,3-thiadiazole (**1**) into a 5-diazomethyl-1,2,3,4-thiatriazole (**2**).[1] If the azide function in (**1**) is replaced by a diazomethyl function, rearrangement should result in the formation of the same thiadiazole ring system, but with a different substitution pattern.[2] This has indeed been found as shown below.

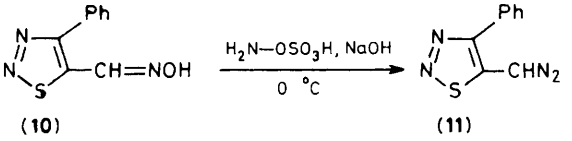
The tosylhydrazone (**3**) (m.p. 168 °C, decomp.) was prepared by a known procedure,[3] and then subjected to the Bamford–Stevens reaction[4] by treatment with diethylamine in dimethylformamide (DMF) at room temperature for 1 h. This furnished, after extraction with chloroform and column chromatography (silica gel, EtOAc–cyclohexane), a yellow liquid in 18% yield, with the following spectral data: i.r. (neat) 2090 (CN_2) and 1690 cm^{-1} (CO); ^1H n.m.r. ($CDCl_3$) δ 1.40 (t, 3H, CH_3), 4.43 (q, 2H, CH_2), and 8.43 (s, 1H, CH); ^{13}C n.m.r. ($CDCl_3$) δ 14.3 (CH_3), 61.4 (CN_2, very weak), 62.9 (CH_2), 139.0 (C-4), 141.6 (C-5), and 163.4 p.p.m. (CO). The presence of an aromatic singlet at δ 8.43 in the ^1H n.m.r. spectrum, as well as a doublet at δ 139.0 p.p.m. ($^1J_{CH}$ 189.1 Hz) for the C-4 ring





Reagents: i, iso-$C_5H_{11}ONO$, EtOK; ii, H_2N–OSO_3H, HO^-, 0 °C.





atom in the undecoupled ^{13}C n.m.r. spectrum, indicates that compound (**5**) is formed instead of (**4**).†

Similarly, when the oxime (**7**) [prepared from the methyl derivative (**6**) and isopentyl nitrite][5] was treated with hydroxylamine *O*-sulphonic acid and base at 0 °C for 1 day, the rearranged thiadiazole (**8**) was isolated in 45% yield. Under the basic conditions required for this Forster reaction,[6] saponification of the ester function occurred. Compound (**8**) exhibited a diagnostic CH ^1H n.m.r. absorption at δ 8.9 [in $(CD_3)_2SO$] and other spectral data in agreement with the assigned structure.

Mechanistically, the observed rearrangement can occur either by a concerted bond-switch mechanism as shown in structure (**4***), or *via* the open-chain intermediate (**9**) in which a thioketone function is flanked by two diazoalkyl functions. Thiocarbonyldiazomethanes have never been isolated, however, but undergo spontaneous cyclization into 1,2,3-thiadiazoles.[7] In our case, the unstable intermediate (**9**) would preferentially cyclize to (**5**).

The stabilizing effect of the carbonyl function on the diazomethyl substituent in (**5**) or (**8**) is the driving force of the isomerization process. Indeed, if this function is replaced by a phenyl group, as in compound (**11**), no isomerization is observed. The 5-diazomethyl-1,2,3-thiadiazole (**11**) was prepared in *ca.* 63% yield by a Forster reaction of the oxime (**10**). It could not be obtained analytically pure, but showed a diazomethyl CH ^1H n.m.r. absorption at δ 5.10.

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† Attempts to prepare (**4**) by substitution of 4-ethoxycarbonyl-5-chloro-1,2,3-thiadiazole with diazomethane failed; no reaction was observed in ether at room temperature.

References

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