SELECTIVE REDUCTION OF 2,5-DIMETHYLENETHIAZOLIDINONE

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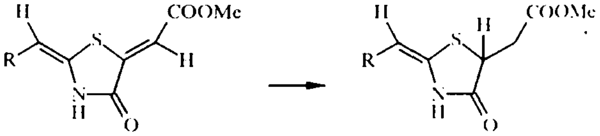
2,5-Dimethylenethiazolidin-4-ones (**1**) are formed by reaction of thioacetamides with dimethylacetylenecarboxylate [1].



1a–d **2a–d**

1, 2 **a** R = COOEt, **b** R = CN, **c** R = $CONH_2$, **d** R = CONHPh

In the present work we have investigated the reduction of compounds **1a-d** with metallic zinc in acetic acid. An individual compound was isolated in 85% yield from the reduction of compound **1a**. In its ^1H NMR spectrum, in addition to the signals of the ethoxy and methoxy group protons, four one-proton signals were observed at 5.43 (s), 4.28 (dd, ^3J = 4.47, ^3J = 8.07 Hz), 3.02 (dd, ^2J = 17.2, ^3J = 4.47 Hz), and 2.93 (dd, ^3J = 8.07 Hz). In the mass spectrum of this compound the molecular ion peak of 259 (25%) was recorded.

On the basis of the spectral data it may be concluded that only one double bond was reduced. Assignment of the exocyclic double bond position in compound **2a** was made by comparing the ^{13}C NMR spectra of compounds **1a** and **2a**. A signal for the methyne group at position 2 of the ring was observed in the spectra of these compounds at 92.8 and 91.7, and for the $C_{(2)}$ atom at 150.5 and 154.3 ppm for compounds **1a** and **2a** respectively. The signal for the $C_{(5)}$ atom was observed at 140.5 for compound **1a** and at 42.7 ppm for compound **2a**. The signal for the methine carbon atom at position 5 for compound **1a** was at 115.8 but that for the methylene carbon of compound **2a** was at 37.5 ppm.

We have therefore shown that a selective reduction of the exocyclic double bond at position 5 of the thiazole ring occurs under the indicated conditions. Analogous results were obtained for compounds **2a-d**.

EXPERIMENTAL

2-Ethoxycarbonylmethylene-5-methoxycarbonylmethylthiazolidin-4-one (2a). Zinc filings (1.5 g) were added to a suspension of compound **1** (1 g) in acetic acid (4 ml), the mixture was stirred at 35°C for 24 h, then water (100 ml) was added, and the mixture stirred for 30 min. The precipitated solid was filtered off, and

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crystallized from alcohol. Yield 0.6 g (65%); mp 130°C. Found, %: C 46.2; H 5.1; N 5.5; S 12.5. $C_{10}H_{13}NO_5S$. Calculated, %: C 46.32; H 5.05; N 5.40; S 12.37.

2-Cyanomethylene-5-methoxycarbonylmethylthiazolidin-4-one (2b). Yield 45%; mp 154°C. ^1H NMR spectrum (DMSO-d_6): 1.8 (1H, br. s, NH); 4.92 (1H, s, =CH); 4.57 (1H, dd, J = 4.88, J = 7.93 Hz, CH); 3.64 (3H, s, OCH_3); 3.12 (1H, dd, J = 4.88, J = 17.19 Hz, CH); 3.08 (1H, dd, J = 17.19, J = 7.93 Hz, CH). Found, %: N 13.0; S 15.3. $C_8H_8N_2O_3S$. Calculated, %: N 13.20; S 15.11.

2-Carbamoylmethylene-5-methoxycarbonylmethylthiazolidin-4-one (2c). Yield 37%; mp >220°C. ^1H NMR spectrum (DMSO-d_6): 12.2 (1H, br. s, NH); 9.28 (1H, br. s, NH); 5.10 (1H, s, =CH); 4.50 (1H, dd, J = 4.9, J = 7.9 Hz, CH); 3.63 (3H, s, OCH_3); 3.11 (1H, dd, J = 4.9, J = 17.3 Hz, CH); 3.00 (1H, dd, J = 17.3, J = 7.9 Hz, CH). Mass spectrum, *m/z* 232 (98). Found, %: N 12.3; S 14.2. $C_8H_{10}N_2O_4S$. Calculated, %: N 12.17; S 13.93.

2-N-phenylcarbamoyl-5-methoxycarbonylmethylmethylenethiazolidin-4-one (2d). Yield 37%; mp 200°C. ^1H NMR spectrum (DMSO-d_6): 11.8 (1H, br. s, NH); 9.75 (1H, br. s, NH); 7.58 (2H, d, J = 7.3 Hz, ArH); 7.25 (2H, dd, J = 7.3, J = 7.4 Hz, ArH); 6.97 (1H, t, J = 7.4 Hz, ArH); 5.79 (1H, s, =CH); 4.18 (1H, dd, J = 4.7, J = 8.5 Hz, CH); 3.64 (3H, s, OCH_3); 3.04 (1H, dd, J = 17.4 Hz, CH); 2.88 (1H, dd, J = 17.4, J = 8.5 Hz, CH). Found, %: N 9.0; S 10.6. $C_{14}H_{14}N_2O_4S$. Calculated, %: N 9.14; S 10.47.

REFERENCES

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