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SHORT COMMUNICATIONS

Reaction of Perhydro-1,3-oxazines with 2-Sulfanylacetic Acid

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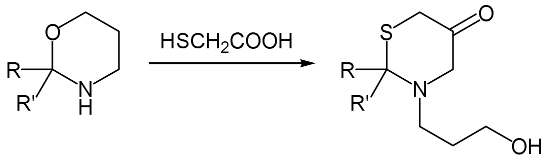
Sulfanylacetic acid is known to react with Schiff bases [1], 2-vinyloxyalkylamines [2], and five-membered O,N-acetals (oxazolidines) [3] to give 1,3-thiazolidin-4-ones. There are no published data on reaction of sulfanylacetic acid with six-membered O,N-acetals.

We examined reactions of perhydro-1,3-oxazines **Ia**–**Ic** with sulfanylacetic acid. The reactions were carried out by heating equimolar amounts of the reactants in benzene with simultaneous removal of water as azeotrope. As a result, 1,3-thiazolidin-4-ones **IIa**–**IIc** were obtained. However, the process is slower than the reaction with five-membered O,N-acetals, the yields of thiazolidin-4-ones **II** being comparable (50–71%).



Ia–Ic **IIa–IIc**

R = R' = H (**a**); RR' = $(CH_2)_5$ (**b**); R = H, R' = Ph (**c**).

The structure of compounds **IIa**–**IIc** was confirmed by the ^{1}H NMR and analytical data. The products were found to inhibit steel corrosion promoted by carbon dioxide and hydrogen sulfide.

3-(3-Hydroxypropyl)-1,3-thiazolidin-4-ones IIa–IIc (*general procedure*). A mixture of 100 ml of benzene, 0.1 mol of perhydro-1,3-oxazine **Ia**–**Ic**, and 0.1 mol of 2-sulfanylacetic acid was heated under reflux in a flask equipped with a Dean–Stark trap until water no longer separated. The products were isolated by vacuum distillation.

3-(3-Hydroxypropyl)-1,3-thiazolidin-4-one (IIa). Yield 11.4 g (71%), bp 170–172°C (2 mm), d_4^{20} = 1.2601, n_D^{20} = 1.5415. ^{1}H NMR spectrum, δ, ppm: 1.74 m (2H, $CH_2C\mathbf{H}_2CH_2$), 3.24 br.s (1H, OH), 3.48 t (2H, OCH_2, ^3J = 6.6 Hz), 3.54–3.56 m (4H, SCH_2CO, NCH_2), 4.41 s (2H, NCH_2S). Found, %: C 44.77; H 6.92; N 8.57; S 19.95. $C_6H_{11}NO_2S$. Calculated, %: C 44.70; H 6.88; N 8.69; S 19.89.

3-(3-Hydroxypropyl)-2,2-pentamethylene-1,3-thiazolidin-4-one (IIb). Yield 14.4 g (63%), bp 235–240°C (5 mm), mp 48–49°C. ^{1}H NMR spectrum, δ, ppm: 1.54–1.92 m [12H, $CH_2C\mathbf{H}_2CH_2$, $(CH_2)_5$], 3.32 br.s (1H, OH), 3.45 t (2H, OCH_2, ^3J = 6.6 Hz), 3.52 s (2H, SCH_2CO), 3.60 t (2H, NCH_2, ^3J = 5.6 Hz). Found, %: C 56.69; H 8.24; N 6.10; S 14.05. $C_{11}H_{19}NO_2S$. Calculated, %: C 57.61; H 8.35; N 6.11; S 13.98.

3-(3-Hydroxypropyl)-2-phenyl-1,3-thiazolidin-4-one (IIc). Yield 14 g (59%), bp 219–222°C (6 mm), mp 63–64°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.40–1.61 m (2H, $CH_2C\mathbf{H}_2CH_2$), 3.00 d.d.d (1H, $NC\mathbf{H}_AH_BCH_XH_Y$, $^3J_{AX}$ = 5.64, $^3J_{AY}$ = 5.64, $^2J_{AB}$ = 14.3), 3.2 br.s (1H, OH) 3.46 d.d.d (1H, $OC\mathbf{H}_AH_BCH_XH_Y$, $^3J_{AX}$ = 4.0, $^3J_{AY}$ = 8.0, $^2J_{AB}$ = 12.0), 3.57 d.d.d (1H, $OCH_A\mathbf{H}_BCH_XH_Y$, $^3J_{BX}$ = 6.0, $^3J_{BY}$ = 6.0, $^2J_{AB}$ = 12.0), 3.66 d.d.d. (1H, $NCH_A\mathbf{H}_BCH_XH_Y$, $^3J_{BX}$ = 5.36, $^3J_{BY}$ = 8.94, $^2J_{AB}$ = 14.3), 3.72 d (1H, $SC\mathbf{H}_AH_BCO$, $^2J_{AB}$ = 15.7), 3.85 d.d (1H, $SCH_A\mathbf{H}_BCO$, $^2J_{AB}$ = 15.7, ^4J = 1.5), 5.58 d (1H, NCH_2S, ^4J = 1.5), 7.3–7.4 m (5H, C_6H_5). Found, %: C 60.84; H 6.39; N 5.85; S 13.66. $C_{12}H_{15}NO_2S$. Calculated, %: C 60.73; H 6.37; N 5.90; S 13.51.

The ^{1}H NMR spectra were recorded on a Bruker DPX-400 spectrometer (400 MHz) at 26°C from solutions in DMSO-d_6 using HMDS as internal reference.

Freshly distilled commercial 2-sulfanylacetic acid was used. Perhydro-1,3-oxazines **Ia**–**Ic** were synthesized by the procedure described in [4]; their purity was no less than 96% (according to the GLC data). The purity of the initial compounds and reaction products was checked by GLC on an LKhM-80 chromatograph equipped with a thermal conductivity detector and a steel column (3 × 3000 mm) packed with 3% of OV-

17 on Inerton Super (0.160–0.200 mm); oven temperature programming from 60 to 300°C at a rate of 4 deg/min; carrier gas helium.

REFERENCES

1. Surrey, A.R., *J. Am. Chem. Soc.*, 1947, vol. 69, p. 2911; Surrey, A.R. and Cutler, R.A., *J. Am. Chem. Soc.*, 1954, vol. 76, p. 578.
2. Kukharev, B.F., Stankevich, V.K., and Klimenko, G.R., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1996, p. 677.
3. Kukharev, B.F., Stankevich, V.K., and Klimenko, G.R., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1997, p. 2221; Kukharev, B.F., Stankevich, V.K., Klimenko, G.R., Kovalyuk, E.N., and Bayandin, V.V., *Zh. Prikl. Khim.*, 2002, vol. 75, p. 680.
4. Pajiness, T.A., US Patent no. 3707541, 1972; *Chem. Abstr.*, 1973, vol. 78, no. 72165.