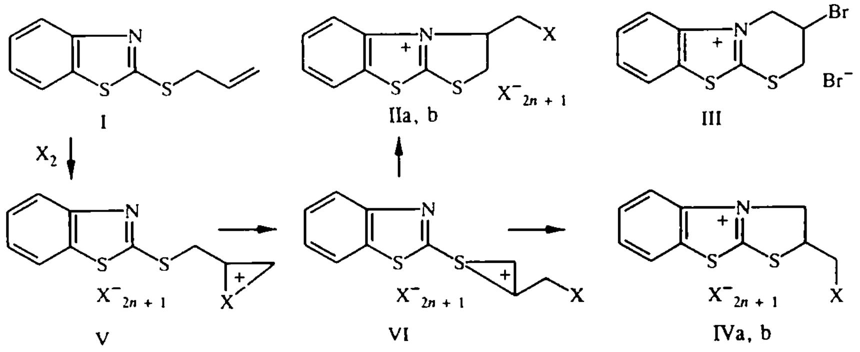
Chemistry of Heterocyclic Compounds, Vol. 34, No. 4, 1998

HALOCYCLIZATION OF 2-ALLYLTHIOBENZOTHIAZOLE

D. G. Kim

Contradictory data is given in the literature on bromocyclization of 2-allylthiobenzothiazole (I). Thus according to data in [1], 3-bromomethyl-2,3-dihydrothiazolo[2,3-*b*]benzothiazolium bromide (IIa) is formed; but according to data in [2], 3-bromo-3,4-dihydro-2H-benzothiazolo[2,3-*b*]-1.3]thiazinium bromide (III) is formed.



IIa, IVa X = Br, n = 0; IIb, IVb X = I, n = 1

We have established that halocyclization of sulfide I occurs with formation of a mixture of 3- and 2-halomethyl-2,3-dihydrothiazolo[3,2-*b*]benzothiazolium halides (IIa, b and IVa, b). Unexpected formation of compounds IVa, b is probably due to the fact that the halogenated ion V is isomerized to the thiiranium ion VI, and compounds IVa, b and IIa, b are formed by intramolecular cyclization of VI.

Evidence for the presence of compounds IIa, b in the mixture comes from the presence in the PMR spectra of a signal from the 3-H proton in the 6 ppm region; evidence for compounds IVa, b comes from signals for the 2-H proton and protons in the NCH_2 group in the 5 ppm region.

Bromocyclization. A solution of 0.1 ml (2 mmoles) bromine in 5 ml CCl_4 was added to a solution of 0.414 g (2 mmoles) sulfide I in 5 ml CCl_4. After 1 h, the mixture of bromides IIa and IVa was filtered. On standing, compound IVa precipitated out of the filtrate. Yield, 0.1 g (13%). T_{mp} 213-215°C. PMR spectrum in $(CD_3)_2SO$: 4.10 (2H, m, CH_2Br); 5.04 (2H, m, NCH_2); 5.15 (1H, m, 2-H); 7.66, 7.77, 8.06, 8.32 ppm (4H, m, H arom.). Found, %: S 17.25; Br 43.76. $C_{10}H_9Br_2NS_2$. Calculated, %: S 17.44; Br 43.60.

Iodocyclization. A solution of 4 mmoles iodine in 10 ml ethanol (2-propanol) was added to a solution of 2 mmoles sulfide I in 10 ml ethanol (2-propanol). The precipitate was dissolved in acetone and precipitated again by diethyl ether. Obtained: triiodides IIb and IVb. T_{mp} 90-110°C (decomp.). PMR spectrum in $(CD_3)_2SO$: (iodide IIb) 3.90-4.70 (4H, m, SCH_2, CH_2I); 5.90 ppm (1H, m, 3-H); (iodide IVb) 3.85 (2H, m, CH_2I); 5.10 (3H, m, 2-H and NCH_2); 7.4-7.90, 8.13, 8.31 ppm (4H, m, H arom.). Found, %: S 8.76, I 71.28. $C_{10}H_9I_4NS_2$. Calculated, %: S 8.96; I 71.03.

REFERENCES

1. M. Kocevar, B. Stanovnik, and M. Tisler, Croat. Chem. Acta, **45**, 457 (1973).
2. N. I. Korotkikh, A. F. Aslanov, and O. P. Shvaika, Khim. Geterotsikl. Soedin., No. 6, 855 (1990).

Chelyabinsk State University, Chelyabinsk 454021, Russia. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, p. 566, April, 1998. Original article submitted February 23, 1998.

0009-3122/98/3404-0505$20.00