Tetrahedron Letters No. 11, pp 895 - 896, 1977. Pergamon Press. Printed in Great Britain.

# RING EXPANSION REACTION IN SUBSTITUTED THIAZOLONES

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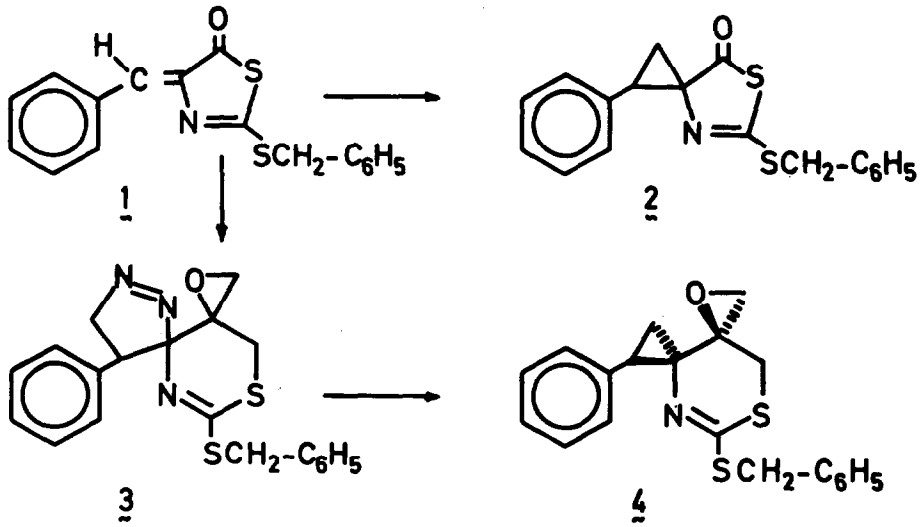
(Received in UK 24 January 1977; accepted for publication 2 February 1977)

As an approach to the synthesis of 1-aminocyclopropanecarboxylic acids, compounds in which we are interested[1], we treated 4-benzylidene-2-benzylthio-5(4H)-thiazolone[2] 1 with diazomethane, obtaining a mixture of two main products, namely the desired spirothiazolone 2 and a second substance 3. After several attempts, we were able to prepare either compound, practically free from each other, just by changing the reaction conditions.

Thus, treatment of 1 with a benzene solution of diazomethane at 35 - 40º yielded 45% of compound 2. This type of reaction, and the subsequent hydrolysis of the spirothiazolones to produce 1-amino-2-arylcyclopropanecarboxylic acids, has been described elsewhere[3]. On the contrary, addition at 0 - 2º of 1 to a large excess of ethereal diazomethane gave compound 3, which crystallized spontaneously during the reaction, in 65% yield.

Here we present the main facts which led us to propose the structure depicted in the scheme for compound 3, which we believe to be of interest in connection with the chemistry of cephalosporins.



Compound 3, $C_{20}H_{19}N_3OS_2$, m.p. 150-1º (dec); IR (KBr, $cm^{-1}$) shows a band at 1595 (s) (C=N) and no significant signal in the 1600-1700 region.

$^1$H-NMR (100 MHz, $Cl_3CD$-TMS, $\delta$) main features: 2.67 (1H, d, J = 12.5 Hz, C-C<u>H</u>H-S), 2.85 (1H, d, J = 4.6, C-C<u>H</u>H-O), 3.32 (1H, m, X portion of ABX system, $J_{AX}$ = 7.2, $J_{BX}$ = 8.4, Ph-C<u>H</u><), 3.38 (1H, m, J = 12.5, J = 1.5, C-CH<u>H</u>-S), 3.56 (1H, m, J = 4.6, J = 1.5, C-CH<u>H</u>-O), 4.8 (2H, m, AB portion of ABX system, $J_{AB}$ = 17.6, -$CH_2$-N=N).

$^{13}$C-NMR (90 MHz, $Cl_3CD$-TMS, ppm), 159.5 (N=C-S), 102.4 (N-C-N), 83.6 (C-N=N), 56.0 (>C-O), 53.2 ($CH_2O$), 46.5 (Ph-CH<), 35.9 (S-$CH_2$-Ph), 31.5 (S-$CH_2$).

By heating compound 3 up to the melting point it loses $N_2$, giving 80% of compound 4, m.p. 101-2º, $C_{20}H_{19}NOS_2$, $M^+$ 353. IR peak at 1595 (s) (C=N). Absence of any significant signal in the 1600-1700 region.

$^1$H-NMR shows, among others, signals at 1.41 (2H, m, AB portion of ABX system, $J_{AB}$ = 5.1, C-C<u>H</u>H-C), 2.43 (1H, m, X portion of ABX, $J_{AX}$ = 9.5, $J_{BX}$ = 7.5, Ph-C<u>H</u>), 2.56 (1H, d, J = 12.0, C-C<u>H</u>H-S), 2.74 (1H, d, J = 4.6, -C<u>H</u>H-O), 2.84 (1H, m, J = 4.6, J = 1.5, -CH<u>H</u>-O), 3.45 (1H, m, J = 12.0, J = 1.5, -CH<u>H</u>-S).

$^{13}$C-NMR: 152.6 (N=C-S), 55.1 (>C-O), 53.6 ($CH_2$-O), 48.6 (>C-N), 35.6 (Ph-C-S), 32.7 (Ph-C<), 30.6 (-$CH_2$-S), 18.6 ($CH_2$ cyclopropane).

The structure of compound 4 is also supported by X-ray studies[4], which point to the configuration outlined in the scheme.

Further studies on the scope and limitations of this reaction and also on the chemistry of analogs of compounds 3 and 4 are in progress.

<u>Acknowledgment</u>: We thank Dr. A. Alemany Soto for INDOR experiments and Dr. M. Rico Sarompas for providing $^{13}$C spectra.

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