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# SYNTHESIS OF BENZOPENTATHIEPINS. REACTIONS OF 1,3-BENZODITHIOLE-2-THIONE AND 1,2-BENZENEDITHIOL WITH ELEMENTAL SULFUR IN LIQUID AMMONIA

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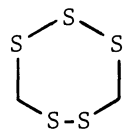
Benzopentathiepins were synthesized by new reaction of 1,3-benzodithiole-2-thiones and 1,2-benzenedithiols with elemental sulfur/liquid ammonia at ambient temperature in high yields.

Many interests of organic sulfur chemists centered on the cyclic polysulfides in the viewpoint of the synthesis of the natural products, for examples, lenthionine(1)[1] and sporidesmin(2).[2] Some procedures for the synthesis



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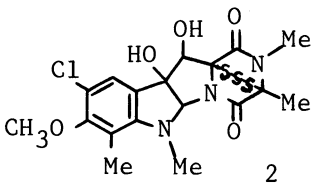

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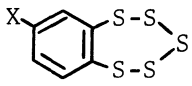
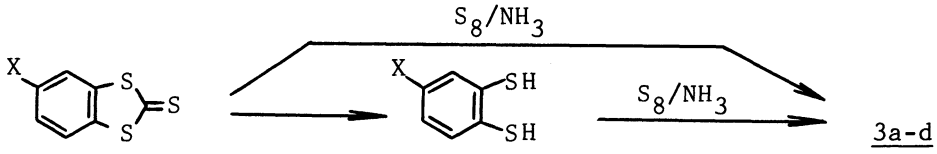


3

of these compounds have been developed in past few years.[3] There have been, however, only a few reports on the synthesis of pentathiepins, which are recognized to have the acaricidal and fungicidal effects.[4] Very recently, Chenard et al. reported the synthesis of benzopentathiepins(3) from benzothiadiazoles with elemental sulfur in the presence of DABCO at high temperature such as 180 °C in moderate yields.[5] Their reports prompted us extremely to disclose the new synthesis of benzopentathiepins(3) by our original methodology, that is, reaction with elemental sulfur/liquid ammonia or amines.[6]

In this communication, we wish to report preliminarily a new synthesis of benzopentathiepins(3) from 1,3-benzodithiole-2-thiones(4) and 1,2-benzenedithiols(5) with elemental sulfur/liquid ammonia at ambient temperature in excellent yields(Scheme 1). Moreover, a remarkable increase of the yields by ad-

dition of nitro compounds such as 1,3-dinitrobenzene in work up was also shown.




3a-d

4a:X=-H d:X=-$NH_2$ 5a-b

b: -Cl e: -$NO_2$

c: -$OCH_3$ Scheme 1.

Typical procedure is as follows. 1,3-Benzodithiole-2-thione(0.5 mmol) (4a)[7] and elemental sulfur(3.0 mg atom) were taken into titanium autoclave and the autoclave was evacuated. Liquid ammonia(30 ml) was charged and then the mixture was stirred at 20 °C for 0.5 h. After completion of the reaction, the liquid ammonia solution of reaction mixture was added dropwise to benzene (80 ml) containing 1,3-dinitrobenzene(0.5 mmol) through a needle bulb and the solution was stirred at room temperature until liquid ammonia was evaporated completely(for about 2 h). Evaporation of benzene under vacuum and subsequent column chromatography on silica gel(Wako gel C-200) using $CCl_4$/hexane as eluent gave desired benzopentathiepin(3a) as a yellow crystals. The products were identified with $^1$H-NMR, IR, MS, and elemental analysis.[8] Compound 3a:IR(KBr) 1420 and 750 $cm^{-1}$; $^1$H-NMR($CDCl_3$) $\delta$= 7.13-7.36(m,2H) and 7.67-7.90(m,2H); MS m/z 236($M^+$). Found: C,30.46; H,1.77%. Calcd for $C_6H_4S_5$: C,30.49; H,1.71%.

Solvents used at the work up of the reaction mixture affected the yield of benzopentathiepin(3), thus, the best yield was obtained when benzene was employed(runs 2,3,and 4). Excepting the case of 6-nitro-benzopentathiepin(3e) where complex products were formed, the generality in the synthesis of 3 was shown in runs 8-12. It should be noted that benzopentathiepin(3a) is obtained in better yield(run 5) from 4 than that from benzenedithiol(5)(run 13) which is generally obtained by solvolysis of 4 (Scheme 1). Our further important finding is that a considerable increase of the yields of 3 has been observed by addition of 1,3-dinitrobenzene to the solvents used at the work up(runs 2,8-11,and 13).[9] In the absence of nitro compounds, unidentified polymer[10] increased. Interestingly, benzopentathiepin(3a) was also obtained by treating the polymer with elemental sulfur in liquid ammonia under similar conditions.

Although the role of 1,3-dinitrobenzene is unclear at present stage, it seems that there are certain equilibriums between 3 and the polymer in the work

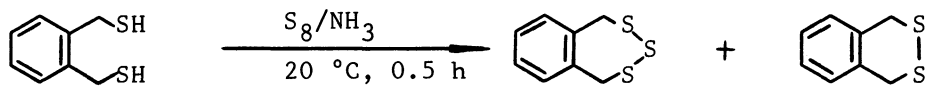
Table 1. Synthesis of benzopentathiepins(3) with $S_8$/ $NH_3$

| Run[a] | Substrate | $S_8$ mg atom equiv | | Solvent[b] | DNB[c] mmol | DNB[c] equiv | Yield of 3[d] | % | Mp(lit.)[5]/°C |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 4a | 3.0 | 6.0 | - | 0 | 0 | 3a | trace | 64 (60) |
| 2 | 4a | 3.0 | 6.0 | $CH_2Cl_2$ | 0.5 | 1 | 3a | 82 (64)[e] | |
| 3 | 4a | 3.0 | 6.0 | $CH_3CN$ | 0.5 | 1 | 3a | 75 (90) | |
| 5 | 4a | 3.0 | 6.0 | benzene | 0.5 | 1 | 3a | 97 (89) | |
| 6 | 4a | 5.0 | 10.0 | benzene | 0.5 | 1 | 3a | 97 | |
| 7 | 4a | 0.5 | 1.0 | benzene | 0.5 | 1 | 3a | 2 | |
| 8 | 4b | 3.0 | 6.0 | $CH_2Cl_2$ | 1.5 | 3 | 3b | 59 (30) | 87 (89) |
| 9 | 4b | 3.0 | 6.0 | benzene | 1.5 | 3 | 3b | 41 (30) | |
| 10 | 4c | 3.0 | 6.0 | benzene | 0.5 | 1 | 3c | 99 (90) | 101 (98) |
| 11 | 4d | 3.0 | 6.0 | benzene | 1.5 | 3 | 3d | 91 (20) | 123 |
| 12 | 4e | 3.0 | 6.0 | benzene | 0.5 | 1 | 3e | 0 | |
| 13 | 5a | 3.0 | 6.0 | benzene | 0.5 | 1 | 3a | 78 ( 5) | |
| 14 | 5b | 3.0 | 6.0 | $CH_2Cl_2$ | 1.5 | 3 | 3b | 54 (19) | |

a) Reaction condition: Reaction temp , 20 °C; Reaction time, 0.5 h; Liquid ammonia, 30 ml ; Substrate, 0.5 mmol; Solvent, 80 ml.
b) These solvents were used in work up. c) 1,3-Dinitrobenzene.
d) Isolated yield based on the substrate. e) Absence of 1,3-dinitrobenzene.

up solution and 1,3-dinitrobenzene can shift the equilibrium to the benzopentathiepin side.[11]

To extend this method to the other compounds, 1,2-bis(mercaptomethyl)benzene(6) as a typical compound was treated with elemental sulfur in liquid ammonia to afford similar seven-membered cyclic trisulfide, 4H,7H-benzo[e]-1,2,3-trithiepin(7),[3,12] in yield of 87% together with six-membered cyclic disulfide, 3H,6H-benzo[d]-1,2-dithiin (8)(trace)(Eq.1). In this reaction, an incorporation of one sulfur atom in the molecule was observed.




6 7 8 (1)

Thus, various benzopentathiepins(3) and analogous cyclic trisulfide(7) were synthesized by this new method, which has a great advantage over precedent

methods in the high yield and mild condition. Further investigations on the detail and applications of this reaction are now in progress in our laboratory.

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8) The products were identified with authentic samples by Chenard.[5)]
9) 1,3-Dinitrobenzene was recovered over 90%.
10) When the yield of 3 was low, the polymer was obtained as an insoluble material in the solvent for chromatography.
11) Actually, we could obtain the polymer by similar treatment of 3 with elemental sulfur in liquid ammonia.
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