Tetrahedron Letters,Vol.30,No.26,pp 3453-3456,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Maxwell Pergamon Macmillan plc

FIRST DIRECT SYNTHESIS OF 4,8-DIALKYLBENZO[1,2-d;4,5-d']BIS[1,2,3]TRITHIOLES AND 6,10-DIALKYL[1,2,3]TRITHIOLO[5,4-h]BENZOPENTATHIEPINS FROM 1,4-DIALKYL-2,3,5,6-TETRABROMOBENZENES

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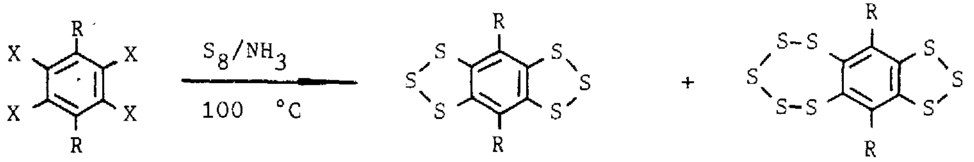
Abstract: New cyclic polysulfides, 4,8-dialkylbenzo[1,2-d;4,5-d']bis[1,2,3]-trithioles (2) and 6,10-dialkyl[1,2,3]trithiolo[5,4-h]benzopentathiepins (3), were directly synthesized by nucleophilic substitution of 1,4-dialkyl-2,3,5,6-tetrahalobenzenes (1) with elemental sulfur in liquid ammonia.

The chemistry on various compounds including many sulfur linkages, cyclic polysulfides, has attracted much attention of organosulfur chemists from the viewpoint of synthesis of natural products.[1] We have also reported the synthesis and reactions of benzopentathiepins as a typical cyclic polysulfides[2] and revealed the versatility[3] of benzopentathiepin in the synthesis of organosulfur and heterocyclic compounds. Furthermore, very recent our paper described the first synthesis of 6,10-dialkoxy[1,2,3]trithiolo[5,4-h]benzopentathiepins from the corresponding 4,8-dialkoxybenzo[1,2-d;4,5-d']bis[1,3]dithiole-2,6-dithiones[4] with elemental sulfur in liquid ammonia.[5] Based on these results, we have successively studied the novel and convenient synthesis of some characteristic cyclic polysulfides. In this paper, we wish to report an unprecedented direct synthesis of noticeable 4,8-dialkylbenzo[1,2-d;4,5-d']bis[1,2,3]-trithioles (2) and 6,10-dialkyl[1,2,3]trithiolo[5,4-h]benzopentathiepins(3) from 1,4-dialkyl-2,3,5,6-tetrahalobenzenes(1) by aromatic nucleophilic substitution[6] with elemental sulfur in liquid ammonia (Scheme 1).

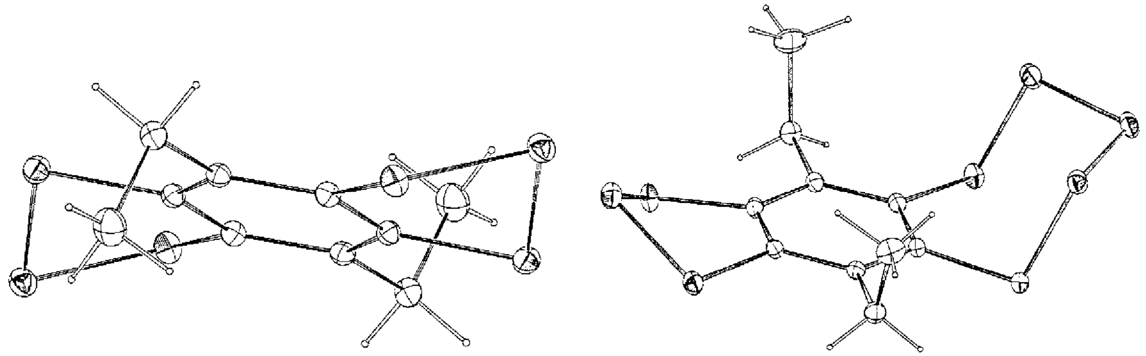


1a R=CH_3 X=Br
b CH_3CH_2 Br

2a Yield=11%
b 27%

3a Yield=70%
b 64%

Scheme 1.



2b 3b

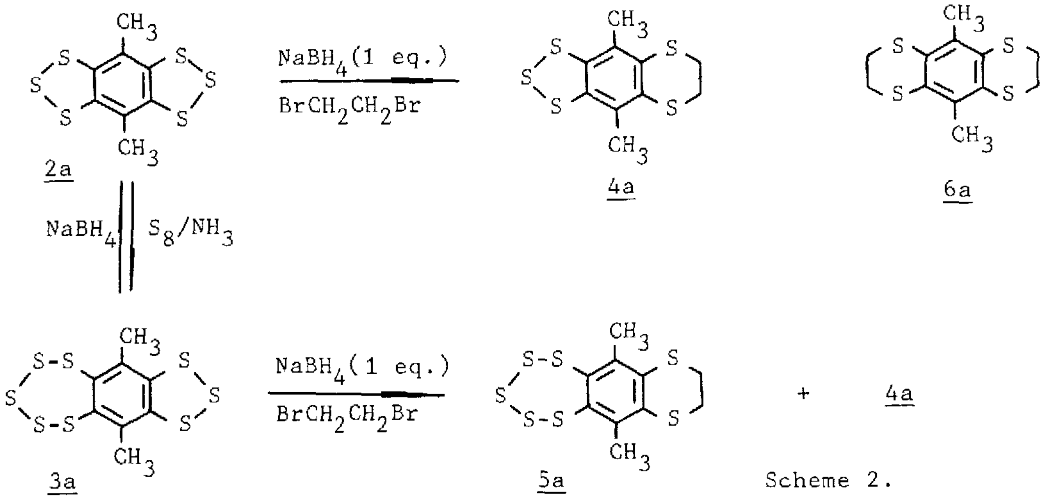
Fig. Structure of 2b and 3b

Typical experimental procedure is as follows. Liquid ammonia (30 ml) was charged into an evacuated titanium autoclave containing 1,4-diethyl-2,3,5,6-tetrabromobenzene (0.5 mmol) and elemental sulfur (25 mg atom) and then the solution was heated at 100 °C for 15 h. The reaction mixture was added into CH_2Cl_2 (200 ml) through needle valve. Then the residue obtained by evaporation of ammonia and solvent was chromatographed on silica gel using CCl_4/hexane (v/v, 1/3) as an eluent giving 2b (37 mg, 23%) and 3b (129 mg, 67%).

2b: Dark red crystals(from CH_2Cl_2); mp 143 °C; IR(KBr) 2950, 1440, and 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.17 (t, 6H, CH_3) and 2.74 (q, 4H, CH_2); MS (70 eV) m/z 322 (M^+). Found: C, 36.95; H, 2.97%. Calcd for $C_{10}H_{10}S_6$: C, 37.24; H, 3.13%.

3b: Reddish brown crystals (from CH_2Cl_2); mp 116 °C; IR (KBr) 2950, 2850, 1440, and 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.20 (t, 6H, CH_3), 2.96 (dq, J=13.6 Hz, J=7.4 Hz, 2H, CH_2), and 3.08 (dq, J=13.6 Hz, J=7.4 Hz, 2H, CH_2); MS (70 eV) m/z 386 (M^+). Found: C, 30.92; H, 2.63%. Calcd for $C_{10}H_{10}S_8$: C, 31.06; H, 2.61%.

It should be surprising that such cyclic polysulfides which have pentathiepins and/or trithiole rings on benzene ring were directly synthesized from aryl halides with elemental sulfur in liquid ammonia, since these reactions were truly unprecedented and especially benzobistrithiole 2 has never been, to our knowledge, synthesized hitherto.7) The whole reaction pathway should be interpreted in terms of nucleophilic substitution of aryl halide with thiolate anion formed from elemental sulfur in liquid ammonia.6) An addition of radical scavenger such as aromatic nitro compounds into the reaction system did not prevent the reaction but the detail of this reaction is not necessarily obvious at present stage. Since 3a was given in 78% yield upon treating 2a with S_8/NH_3 at 25 °C for 5 h, it seems that there is an interconversion between 2 and 3 in this reaction system. Based on the crystallography,8) the structure of 2b was found to be all trans conformation for both two trithiole rings and ethyl groups on benzene ring and to be nearly consistent with known benzotrithiole.[7] Whereas, a butterfly-like conformation was observed for the whole structure of 3b as shown in Fig. 1. The ^{1}H NMR study on 2b and 3b gave interesting results that the methylene proton of ethyl group in 2b showed usual quartet pattern (2.74 ppm), while double quartet for 3b was observed at lower field (2.96 and 3.08 ppm) than that of 2b. The free rotation of ethyl group in 3b may be inhibited by steric bulkiness of two neighboring sulfur atoms. The alkyl substituents influenced the ratio of 2 : 3 as shown in Scheme 1. Thus, the introduction of bulky substituent, ethyl group, increased the yield of 2b. These results suggest that the bulkiness of substituent in 1,4-position of benzene ring can control the ring size of such cyclic polysulfide.[4]



Scheme 2.

The products, 2 and 3, were exposed under some reactions to confirm the chemical properties as shown in Scheme 2. The reduction of 2a with sodium borohydride followed by alkylation with 1,2-dibromoethane afforded an interesting benzotrithiole 4a[9] in 35% yield. Whereas 3a was converted to 2a (68%) by the reaction with sodium borohydride. It should be noted that the alkylation 3a with 1,2-dibromoethane after reduction with sodium borohydride gave new compounds, benzopentathiepin 5a,[10] in 20% yield together with 4a (27%), since 4a and 5a were partial reduction products of cyclic polysulfide moiety of 2a and 3a under basic conditions. 9,10-Dimethyl-2,3,6,7-tetrahydro-1,4,5,8-tetrathiaanthracene (6a)[6] was also obtained in high yields by exhaustive reductions of 2a, 3a, 4a, and 5a followed by alkylation.

The further applications of this process for synthesis of some cyclic polysulfides are now under investigation in our laboratory.[11]

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8. X-ray crystallographical data. 2b: M.F.=$C_{10}H_{10}S_6$, M.W.=322.55, monoclinic, space group $P2_1/c$, a=14.755(1), b=8.620(1), c=5.191(1)Å, β=89.00(1)°, V=660.1(3)$Å^3$, Z=2, Dc=1.623g/cm^3, μ(MoKα)=9.658cm^{-1}, final R-factor=0.0425 (Rw=0.0429) for 1654 reflections with Fo>3σ(Fo) out of 1874 measured reflections. 3b: M.F.=$C_{10}H_{10}S_8$, M.W.=386.67, monoclinic, space group $P2_1/n$, a=14.211(1), b=9.5151(1), c=11.254(1)Å, β=93.31(1)°, V=1519.3(3)$Å^3$, Z=4, Dc=1.690 g/cm^3, μ(MoKα)=11.092 cm^{-1}, final R-factor=0.0419(Rw=0.0409) for 3485 reflections with Fo>3σ(Fo) out of 3710 measured reflections. Table of the structural data are available from the Cambridge Crystallographic Data Center.
9. 4a: Orange crystals (from CH_2Cl_2); mp 157 °C; IR(KBr) 2890, 1380, 1260, and 990 cm^{-1}; ^1H NMR($CDCl_3$) δ=2.39(s,6H,CH_3) and 3.20(s, 4H, CH_2); MS(70 eV) m/z 290(M^+). Found: C, 41.09; H, 3.33%. Calcd for $C_{10}H_{10}S_5$: C, 41.35; H, 3.47%.
10. 5a: Pale yellow crystals(from CH_2Cl_2); mp 171 °C; IR (KBr) 2900, 1375, 1290, and 985 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.64 (s,6H,CH_3) and 3.30(s,4H,CH_2); MS(70 eV) m/z 354 (M^+). Found: C,33.70; H,2.79%. Calcd for $C_{10}H_{10}S_7$: C,33.87; H,2.84%.
11. We could directly obtain benzopentathiepin[2)] in 8% yield from 1,2-diiodobenzene with elemental sulfur in liquid ammonia at 120 °C for 36h.

(Received in Japan 19 April 1989)