3-ARYL-3*H*-1,2-BENZODITHIOLES. SYNTHESIS AND REACTION WITH DICHLOROCARBENE AND CARBENOID

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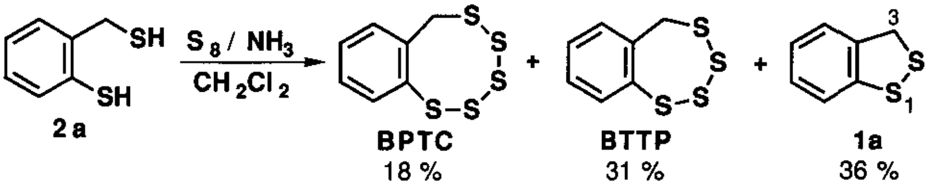
Abstract - New stable 3*H*-1,2-benzodithiole derivatives, 3-aryl-3*H*-1,2-benzodithioles, were synthesized. While the reaction of the 3-aryl-3*H*-1,2-benzodithioles with CH_2I_2-Et_2Zn gave methylene-inserted products 4-aryl-2,4-dihydro-1,3-benzodithiins, the reaction with dichlorocarbene afforded unexpected products 2-chloro-3-arylbenzo[*b*]thiophenes.

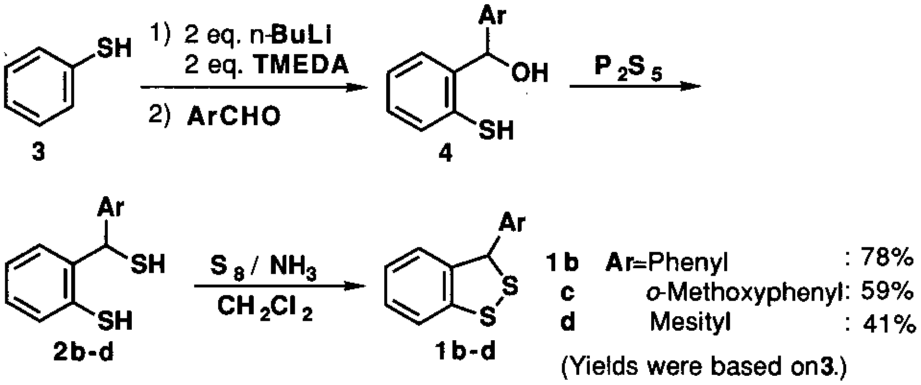
Recently, the attention of many organic sulfur chemists has been directed to study of the biological activity as well as the unique reactivity of cyclic polysulfides such as benzopentathiepin.[1] We have succeeded in the synthesis of a variety of cyclic polysulfides by the reaction of the corresponding dimercaptanes with elemental sulfur / ammonia and have examined their reactivities to give many heterocycles involving sulfur atoms.[2] Our current interest has focused on the chemistry of new types of cyclic polysulfides containing a benzylmethylene group in the polysulfides ring, e.g., 6*H*-benzo[*g*]-1,2,3,4,5-pentathiocin (**BPTC**), 5*H*-benzo[*f*]-1,2,3,4-tetrathiepin (**BTTP**), and 3*H*-benzo-1,2-dithiole (**1a**).[3] Here we wish to report a synthesis of new stable 3*H*-1,2-benzodithiole derivatives having an aryl substituent at 3-position[4] and the reactions with electrophilic agents such as dichlorocarbene and carbenoid.



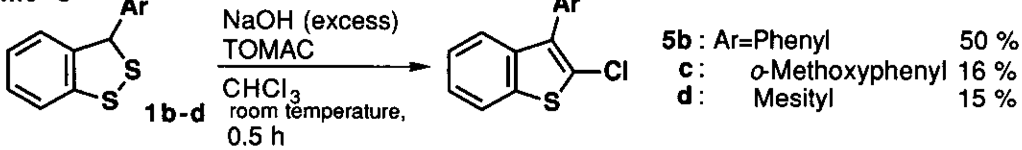
Scheme 1

Treatment of the alcohol (**4**), which was derived from thiophenol (**3**) by ortho-lithiation[5] followed by reaction with aldehyde, with P_2S_5 afforded dimercaptanes (**2b-d**). The desired 3-aryl-3*H*-1,2-benzodithioles (**1b-d**) were obtained by cyclization of **2b-d** with S_8 / NH_3 in CH_2Cl_2[2] (Scheme 2). In contrast to the reaction of 2-mercaptomethylbenzenethiol (**2a**) with S_8 / NH_3 to give a mixture of **BTTP**, **BPTC**, and **1a**[3] (Scheme 1), the same treatment of **2b-d** afforded only 1,2-benzodithioles (**1b-d**). These results suggest that in the reaction the introduction of a suitable substituent at the benzyl position in **2a** controls the ring size of the cyclic polysulfides produced by the reaction of **2** with S_8 / NH_3. The structures of all new 3*H*-1,2-benzodithioles (**1b-d**) were assigned on the basis of ^1H nmr, ir, mass spectrometry, and elemental analysis.[6] Since the repulsion between sulfur-sulfur lone pair electrons in the 1,2-dithiole ring leads to easy cleavage of the sulfur-sulfur bond, compound (**1a**) is unstable even at room temperature and easily polymerizes. Therefore, it is difficult to isolate **1a** in pure state[7] and the chemistry of **1a** has not been studied in detail so far.[8] Interestingly, in contrast to **1a**, 3*H*-1,2-benzodithioles (**1b-d**) are extremely stable cyclic disulfides. Consequently, **1b-d** are suitable compounds to study the chemistry of the 3*H*-1,2-benzodithioles.[9] To examine the reactivity toward electrophiles, **1b-d** were exposed to dichlorocarbene and carbenoid.[10] Thus, treatment of **1b-d** with excess NaOH and trioctylmethylammonium chloride (TOMAC) in $CHCl_3$ at room temperature for 0.5 h gave the unexpected product, 2-chloro-3-aryl-benzo[*b*]thiophenes (**5b-d**) (Scheme 3). **5b**; pale yellow oil; ^1H nmr ($CDCl_3$) δ 6.90-7.90 (m); ir (neat) 2950, 1425, 1010, and 750 cm^{-1}; ms m/z calcd for $C_{14}H_9ClS$ 244.0113, obsd 244.0085.

Scheme 2



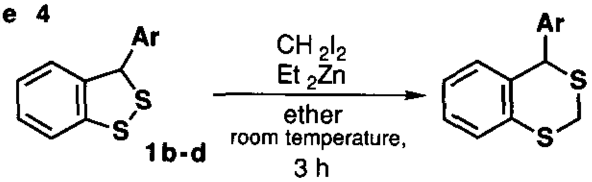
Scheme 3



On the other hand, treatment of **1b-d** with CH_2I_2 and Et_2Zn (0.98 M n-hexane solution) in ether afforded methylene-inserted products 4-aryl-1,3-benzodithianes (Scheme 4). **6b**; pale yellow oil; ^1H nmr ($CDCl_3$) δ 3.82

(s, 2H, -CH_2-), 5.23 (s, 1H, -CH<), 6.73-7.63 (m, 9H, arom); ir (neat) 2920, 1439, and 706 cm^{-1}; ms m/z calcd for $C_{14}H_{12}S_2$ 244.0380, obsd 244.0328.

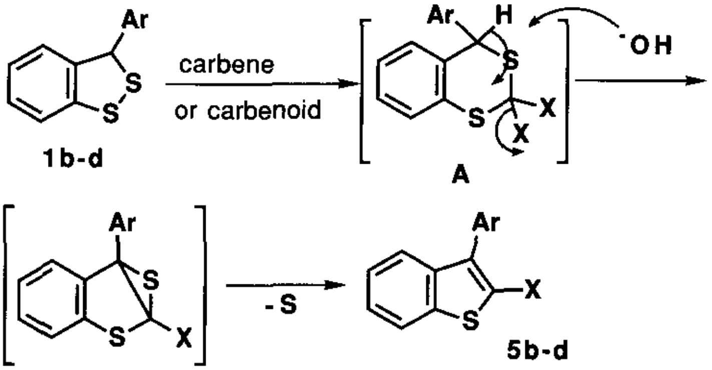
Scheme 4



6b : Ar=Phenyl 49 %
c : o-Methoxyphenyl 18 %
d : Mesityl 26 %

From these results, a plausible reaction pathway to form **5** from **1** with dichlorocarbene is shown in Scheme 5.

Scheme 5



The dichlorocarbene-inserted product (**A**), which was formed from **1** with dichlorocarbene, is deprotonated with excess NaOH followed by ring-contraction accompanied with elimination of chloride and aromatization accompanied with desulfurization to give **5**.

Further study on the reactivity of the 3*H*-1,2-benzodithioles (**1b-d**) is now in progress.

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6. **1b** (Ar=Phenyl); Yellow oil; ^{1}H nmr ($CDCl_3$) δ 5.96 (s, 1H, Ph-CH) and 6.86-7.60 (m, 9H, arom); ir (neat) 3000, 1570, 1440, 730, and 690 cm^{-1}; ms (m/z) 230(M$^+$); uv λmax (MeCN) 367.5 nm (ε 407); Anal. Calcd for $C_{13}H_{10}S_2$ C, 67.58; H, 4.67. Found: C, 67.71; H, 4.33. **1c** (Ar=*o*-Methoxyphenyl); Yellow needles; mp 97°C (from n-hexane); ^{1}H nmr ($CDCl_3$) δ 3.88(s, 3H, -OCH_3), 6.30(s, 1H, -CH-), and 6.60-7.45(m, 8H, arom); ir (neat) 2925, 1489, 1461, 1248 and 747 cm^{-1}; ms (m/z) 260(M$^+$); uv λmax (MeCN) 364.5 nm (ε 322); Anal. Calcd for $C_{14}H_{12}OS_2$ C, 64.58; H, 4.65. Found: C, 64.44; H, 4.67. **1d** (Ar=Mesityl); Yellow oil; ^{1}H nmr ($CDCl_3$) δ 2.15(s, 3H, *o*-CH_3), 2.25(s, 3H, *p*-CH_3), 2.42(s, 3H, *o*-CH_3), and 6.50-7.20(m, 5H, Ms-CH- and arom); ir (neat) 2918, 1609, 1438, and 743 cm^{-1}; uv (MeCN) λmax 393.5 nm (ε 507); ms m/z calcd for $C_{16}H_{16}S_2$ 272.0693, obsd 272.0696.

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9. To obtain the structural information, the theoretical calculations of **1a-d** were carried out using MM2(77) and MOPAC Ver.5.01 [MOPAC Ver. 5.00 (QCPE No. 445), J. J. P. Stewart, QCPE Bull., 1989, 9, 10; T. Hirano, JCPE Newsletter, 1989, 1, 36; Revised as Ver. 5.01 by J. Toyoda, for Apple Macintosh] programs. The calculation results are shown below.

Dithiole	Calcd. S-S bond length (Å)	Calcd. CSSC dihedral angle (deg.)	Energy level of HOMO (eV)
1a	2.017	36.9	-8.59
1b	2.015	36.6	-8.53
1c	2.014	36.2	-8.39
1d	2.011	32.1	-8.40

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