

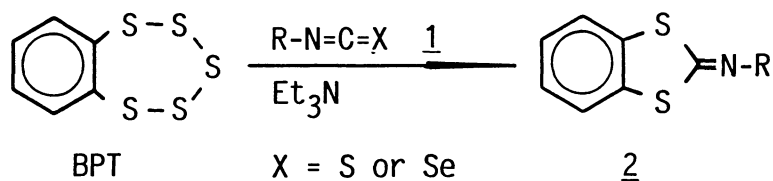
Chemistry of Benzopentathiepin.
Formation of 2-Imino-1,3-benzodithioles from
Alkyl or Aryl Isochalcogenocyanates with Benzopentathiepin

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Various 2-imino-1,3-benzodithioles were synthesized in good yields by the reaction of alkyl or aryl isochalcogenocyanates, $R-N=C=X$ ($X=S$ or Se), with benzopentathiepin in the presence of triethylamine.

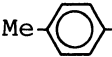
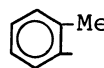
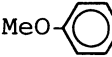
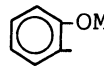
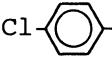
Recently, the synthetic versatility of cyclic polysulfides having many sulfur-sulfur linkages in the molecules has been recognized in organosulfur and heterocyclic chemistry.¹⁾ Our current interest was directed to the synthesis and reactions of cyclic polysulfides such as benzopentathiepin (BPT) and the related compounds.²⁾ Acid- or base-induced reactions of BPT with olefins produce many heterocycles containing sulfur atom.³⁾ We have now found that the reactions of heterocumulenes, alkyl or aryl isochalcogenocyanates 1 ($R-N=C=X$, $X = S$ or Se), with BPT in the presence of Et_3N as a base give corresponding 2-imino-1,3-benzodithioles (2) in good yields (Scheme 1). In this paper, a plausible reaction pathway is also proposed.



Scheme 1.

Various 2-imino-1,3-benzodithioles 2a-i were obtained in moderate to good yields by treatment of alkyl and aryl isochalcogenocyanates 1a-i with BPT in the presence of triethylamine, as shown in Table 1 (Runs 1-4 and 10-14). On the whole, the reaction of aromatic isothiocyanates is faster than that of alkyl isothiocyanates 1a-c and is accelerated by the electron-

Table 1. Synthesis of 2-imino-1,3-benzodithiole 2

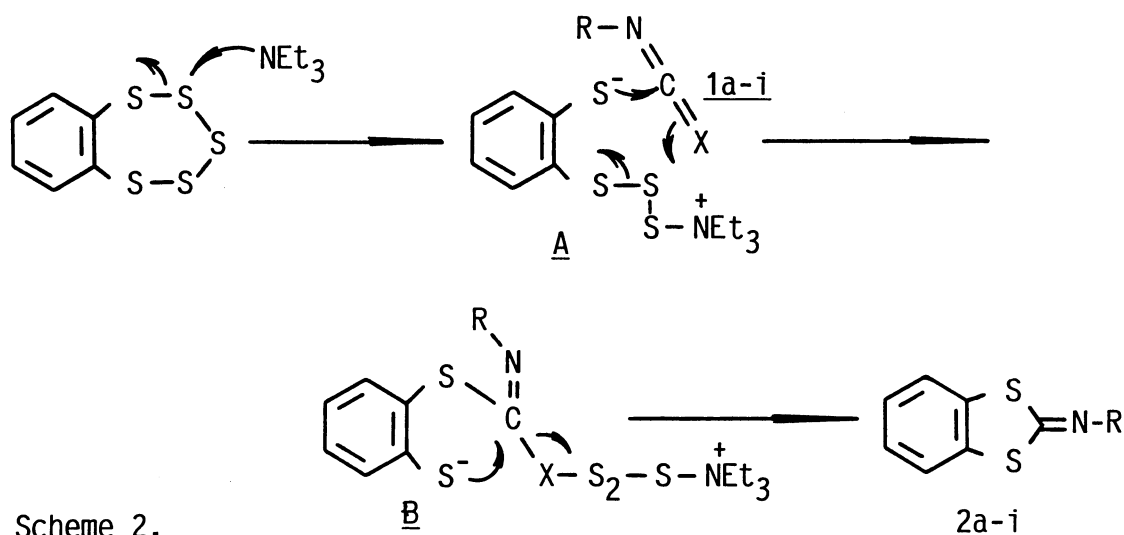
Run ^{a)}	R-N=C=X		<u>1</u>	Base	React.		Yield/% of <u>2</u> ^{b)}	Mp/°C (lit)
	R	X			temp/°C	time/h		
1	Me-	S	<u>1a</u>	Et ₃ N	60	8	81 <u>2a</u>	56 (52) ⁴⁾
2	Et-	S	<u>1b</u>	Et ₃ N	60	12	59 <u>2b</u>	48
3	n-Pr-	S	<u>1c</u>	Et ₃ N	60	12	47 <u>2c</u>	52
4	Ph-	S	<u>1d</u>	Et ₃ N	60	2	78 <u>2d</u>	66 (69) ⁴⁾
5	Ph-	S	<u>1d</u>	EtONa ^{c)}	r.t.	2	72 <u>2d</u>	
6	Ph-	S	<u>1d</u>	NaH ^{d)}	r.t.	24	12 <u>2d</u>	
7	Ph-	S	<u>1d</u>	Et ₃ N/PPh ₃ ^{e)}	80	24	14 <u>2d</u>	
8	Ph-	Se	<u>1d-Se</u>	Et ₃ N/PPh ₃ ^{e)}	80	1	80 <u>2d</u>	
9	Ph-	O	<u>1d-O</u>	Et ₃ N	60	24	no reaction	
10	Me- 	S	<u>1e</u>	Et ₃ N	60	6	77 <u>2e</u>	65
11	 -Me	S	<u>1f</u>	Et ₃ N	60	6	71 <u>2f</u>	62
12	MeO- 	S	<u>1g</u>	Et ₃ N	60	5	74 <u>2g</u>	76
13	 -OMe	S	<u>1h</u>	Et ₃ N	60	5	86 <u>2h</u>	89
14	Cl- 	S	<u>1i</u>	Et ₃ N	60	1	84 <u>2i</u>	103

a) Reaction conditions: 1, 0.5 mmol; BPT, 0.5 mmol; base, 1.5 mmol; solvent (DMSO), 1 ml. b) Isolated yield based on BPT. c) Base, 0.5 mmol. d) Base, 0.5 mmol. e) Et₃N, 0.5 mmol; PPh₃, 1.5 mmol; benzene, 15 ml.

withdrawing group (1i) (Run 14). Some bulky substrates having a methyl or a methoxy substituent at ortho position (1f and 1h) had no affect on the result. Among the bases used in the present reaction, Et₃N and EtONa gave favorable results (Runs 4 and 5). We chose DMSO after examination of various solvents. Phenyl isoselenocyanate 1d-Se⁵⁾ and phenyl isocyanate 1d-O were also examined under the same conditions. Phenyl isocyanate 1d-O did not react with BPT at 80 °C (Run 9) but 1d-Se did immediately in the presence of Et₃N to yield phenyl isothiocyanate 1d quantitatively via an exchange of selenium with sulfur.⁶⁾ In order to avoid such exchange, the reaction of 1d-Se was carried out in the presence of triphenylphosphine as a

sulfur trapper. However, the same product 2d was consequently obtained (Run 8). It should be noted that 1d-Se reacted with BPT to give 2d (1 h, 80%) more easily (Run 8) than 1d (24 h, 14%) (Run 7), since these results are very important in considering the reaction pathway.

In the initial step of this reaction, the sulfur-sulfur bond of BPT is cleaved by nucleophilic attack with triethylamine (Scheme 2). The thiolate anion A formed adds to thio- or selenocarbonyl carbon of 1 to afford polysulfide intermediate B through the seven-membered transition state. Then the intermediate B cyclizes to product 2. Accordingly, BPT functions as a 1,2-benzenedithiolate anion synthon in this reaction. Interestingly, the use of 1,2-benzenedithiol as a reagent instead of BPT under the same condition resulted in the formation of 2d in only 20% yield (cf. Run 4 in Table 1).⁷⁾



In conclusion, we have succeeded in the efficient preparation of various 2-imino-1,3-benzodithioles by the novel reactions of alkyl or aryl isochalcogenocyanates with BPT in the presence of Et_3N . Since, so far, four procedures for the synthesis of 2-imino-1,3-benzodithioles have been reported,^{4,8)} our method is added to the known reactions. Moreover, the present reaction has extended the versatility of cyclic polysulfides in the fields of synthetic chemistry. Based on this successful reaction, further investigation on reactions of other heterocumulenes such as $-\text{P}=\text{C}=\text{N}-$, $-\text{P}=\text{C}=\text{P}-$, and $\text{>C}=\text{C}=\text{S}$ with BPT is now under progress in our laboratory.

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