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CONVENIENT SYNTHESIS OF 1,2,4-BENZOTRITHIINS FROM BENZOPENTATHIEPIN WITH PHOSPHORUS YLIDE

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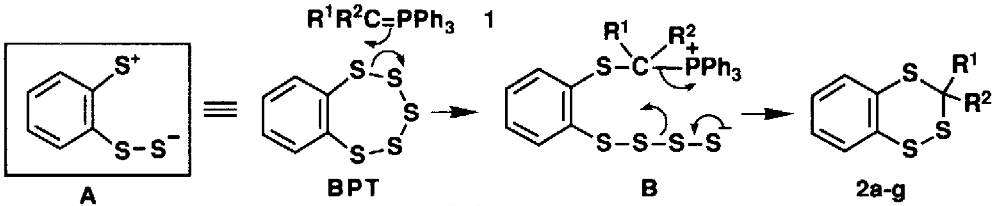
Abstract: Novel 1,2,4-benzotrithiins were synthesized in satisfactory yields by treatment of benzopentathiepin with alkylidenephosphoranes. In this reaction, benzopentathiepin was found to serve as a 1,5-dipole synthon.

Recently a new field in organic sulfur chemistry has been developed, focussing on cyclic polysulfides such as benzopentathiepin (**BPT**) and 5H-benzo[f]-1,2,3,4-benzotetrathiepin, particularly in the synthesis of heterocyclic compounds[1] and sulfur-transfer reaction.[2] In the course of study on the reactions of cyclic polysulfides, our interest was directed to the reactions of cyclic polysulfides with phosphorus ylides.[3] We have now found a novel synthesis of 1,2,4-benzotrithiins (**2**) from **BPT** with phosphorus ylides, alkylidenephosphoranes (**1**) (Scheme 1).

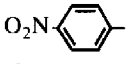
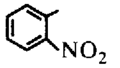
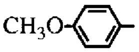
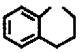


Scheme 1

A typical procedure is as follows. A solution of freshly prepared 4-methoxybenzylidenetriphenylphosphorane (**1e**, 0.5 mmol) from 4-methoxybenzyltriphenylphosphonium chloride (0.5 mmol) with sodium hydride (0.5 mmol) in THF (3 ml) was added dropwise to a solution of **BPT** (0.5 mmol) in benzene (10 ml) at room temperature and then the solution was stirred for 12 h. After the usual work-up, the obtained reaction mixture was chromatographed on silica gel using CCl_4 as an eluent to give 3-(4-methoxyphenyl)-1,2,4-benzotrithiin (**2e**, 34%).[4] These results are summarized in Table1.

All reactions proceeded smoothly to give **2a-g** as a product in satisfactory yields together with triphenylphosphine sulfide. As the base used in the formation of **1** from the corresponding phosphonium halide, EtONa and t-BuOK, besides NaH, were also employed. A stable 9-fluorenilidenetri-phenylphosphorane **1f** was isolated and subjected to the reaction with **BPT** at room temperature, to afford the corresponding 1,2,4-benzotrithiin **2f** in 75% yield (Run 7). Both 1,2,4-benzotrithiins having electron-with-drawing (**2c** and **2d**) and electron-donating (**2e**) groups were obtained in satisfactory yields. Two sterically hindered benzotrithiins, **2f** and **2g**, were also synthesized in high yields as shown in Table1. Based on the fact for the formation of 1,2,4-benzotrithiin **2** and triphenylphosphine sulfide, this reaction is conceived to be initiated by the thiophilic attack of carbanion of **1** to the sulfur atom adjoining benzene of **BPT**, to form intermediate **B** (Scheme 1). The

Table 1.

Run[a)]	$Ph_3P=CR^1R^2$		**1**	Reaction		Yield of $\mathbf{2}^{b)}$	
	R^1	R^2		temp/ °C	time/ h	%	
1	Ph	Ph	**1a**	r.t.	1.5	86	**2a**
2	H	Ph	**1b**	70	12	51	**2b**
3	H		**1c**	r.t.	12	52	**2c**
4	H		**1d**	r.t.	12	38	**2d**
5	H		**1e**	r.t.	12	34	**2e**
6			**1f**	r.t.	12	75	**2f**
7			**1g**	r.t.	12	82	**2g**

a) Reaction conditions: **1**, 0.5 mmol; **BPT**, 0.5 mmol. b) Isolated yields based on **BPT**

cyclization by intramolecular nucleophilic attack of thiolate anion to the carbon in **B** after release of two sulfur atoms, which are trapped with triphenylphosphine to give triphenylphosphine sulfide, affords the desired **2**. The formation of thiocarbonyl compound was not observed in this reaction.[5] Hence, **BPT** was found to serve as a 1,5-dipole synthon, **A** (Scheme 1).

Up to date, there have been some reports on the reactions of phosphorus ylide with sulfur compounds involving elemental sulfur.[6] We could not, however, find any example for the reaction of phosphorus ylide with cyclic and acyclic polysulfides except for disulfide. On the other hand, for the synthesis of 1,2,4-trithiin[7] and 1,2,4-benzotrithiin,[8] only two methods have been reported. Accordingly, the present reaction should be a convenient procedure for providing 1,2,4-benzotrithiins. Further study on the chemical behavior and the synthetic utility of the obtained **2** is now in progress in our laboratory.

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3. The sulfurization of phosphorus ylides with 5H-benzo[f]-1,2,3,4-tetrathiepin gives the corresponding thiocarbonyl compounds. R. Sato and S. Satoh, *Synthesis*, in press.
4. Compound **2e**: Colorless crystals from ether; mp. 137 °C; IR (KBr) 2910, 1600, 1500, 1240, 1020, and 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.83 (s, 3H), 5.96 (s, 1H), and 6.82-7.60 (m, 8H); MS (20 eV) m/z 292 (M^+). Anal. Calcd for $C_{14}H_{12}S_3$: C, 57.50; H, 4.14%. Found: C, 57.05; H, 4.09%.
5. A cycloadduct, thiapyrane, was not formed upon addition of butadiene into the reaction system.[3]
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