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Novel Formations of Unsymmetrical 1,2,5-Benzotrithiepins from Olefins and Benzopentathiepin in the Presence of Lewis Acid. Benzopentathiepin as a Novel 1,5-Dipole Synthon

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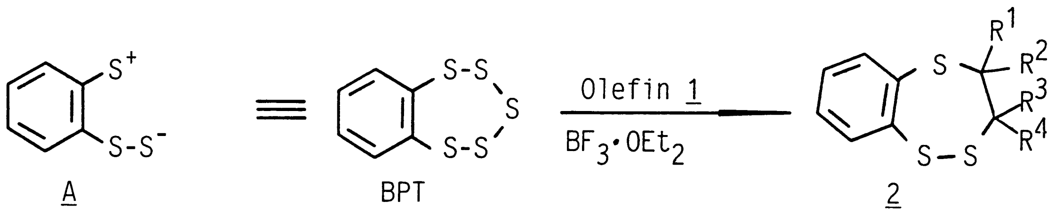
Some unsymmetrical 1,2,5-benzotrithiepins were synthesized in moderate to good yields by the novel reactions of various olefins with benzopentathiepin (BPT) in the presence of a Lewis acid, trifluoroborane etherate. In this reaction, BPT was found to serve as a 1,5-dipole synthon.

Some cyclic polysulfides[1)] such as benzopentathiepins[2)] containing many sulfur linkages in a molecule have been recently studied in the interests of the structure and reactivity.[3)] Moreover, recent attention has been centered on a new field of organosulfur chemistry, and thus, several reports on the sulfur-transfer reactions using cyclic polysulfides have appeared.[4)] We also reported the versatility of benzopentathiepin (BPT) as a sulfurization reagent[5)] and as a 1,4-dication synthon for synthesis of heterocycles such as unsymmetrical thianthrenes.[6)] These results encouraged us to investigate further the synthetic utility of BPT. Here, we wish to report new reactions of BPT with olefins in the presence of Lewis acid, $BF_3 \cdot OEt_2$, affording 1,2,5-benzotrithiepins (2), where BPT serves as a novel 1,5-dipole synthon A (Scheme 1). Although the synthesis of symmetrical 1,2,5-trithiepins,[7)] which show a certain fungicidal effect,[8)] has been reported, there is, to our knowledge, no investigation on synthesis of unsymmetrical ones.

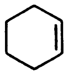
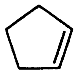
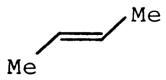
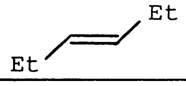


Scheme 1.

Typical procedure is as follows. To a solution of BPT (0.5 mmol) and cyclohexene (1a, 1.0 mmol) in dichloromethane (5 ml) was added $BF_3 \cdot OEt_2$ (0.5 mmol) and the solution was stirred at 40 °C for 24 h. The reaction was quenched with ice-cold water and then the mixture was extracted with dichloromethane (20 ml). The residue was chromatographed on silica gel by using chloroform as an eluent to give cyclohexano[c][1,2,5]benzotrithiepin (2a) (81%). 2a: Mp 59 °C (from hexane); IR (KBr) 2940, 2870, 1450, 1330, 1200, 1050, and 770 $\mathrm{cm^{-1}}$; ^{1}H NMR ($\mathrm{CDCl_3}$) δ = 1.05-1.60 (m, 4H), 1.73-1.93 (m, 2H), 1.93-2.12 (m, 1H), 2.12-2.30 (m, 1H), 2.90-3.18 (m, 2H), 7.13-7.35 (m, 2H, arom), and 7.56-7.85 (m, 2H, arom); MS (70 eV) m/z 254 (M^+). Found: C, 56.78; H, 5.53%. Calcd for $C_{12}H_{14}S_3$: C, 56.65; H, 5.55%.

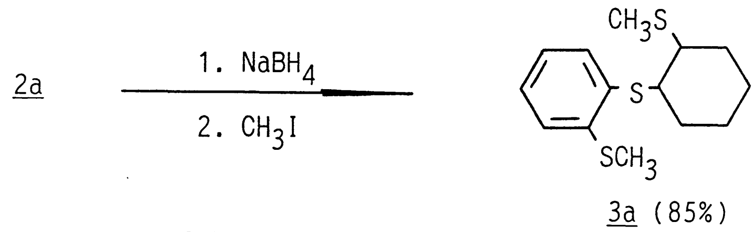
As shown in Table 1, BPT reacted with some olefins in the presence of $BF_3 \cdot OEt_2$ giving unsymmetrical 1,2,5-benzotrithiepins 2. Other Lewis acids, such as $AlCl_3$, $TiCl_4$, and $SnCl_4$ were not so effective as $BF_3 \cdot OEt_2$. The optimization in the reaction of cyclohexene was achieved when 1a (1.0 mmol) was allowed to react with BPT (0.5 mmol) in the presence of $BF_3 \cdot OEt_2$ at 40 °C for 24 h (Runs 1-4). The reaction of 4 equivalent of 1a (2.0 mmol) with BPT (0.5 mmol) gave a trace of 2a; an unidentified complex mixture was formed by further reaction of the product 2a with excess 1a in the presence of $BF_3 \cdot OEt_2$ (Run 3).

Table 1. Reactions of Olefins with BPT

Run$^{a)}$	Olefin	1	(mmol)	Conditions		Yield/% of 2$^{b)}$		Mp/°C
				Temp/°C	Time/ h			
1		1a	(0.5)	r.t.	48	37	2a	59
2		1a	(1.0)	r.t.	48	69	2a	
3		1a	(2.0)	r.t.	40	trace	2a	
4		1a	(1.0)	40	24	81	2a	
5		1b	(1.0)	35	120	68	2b	60
6		1c	(1.0)	40	72	58	2c	oil
7		1d	(1.0)	35	72	39	2d	oil

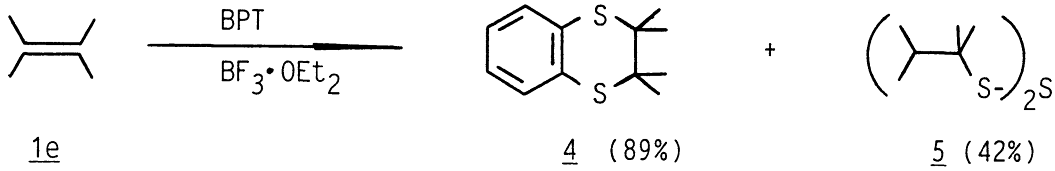
a) BPT, 0.5 mmol; $BF_3 \cdot OEt_2$, 0.5 mmol; CH_2Cl_2, 5 ml.
b) Yield based on BPT.

The structure of 2a was confirmed by the reduction with sodium borohydride followed by the alkylation with methyliodide (Scheme 2), 2-(methylthio)phenyl 2-(methylthio)cyclohexyl sulfide (3a) being obtained in 85% yield. These results show that 2a has a sulfide and a disulfide groups, both linked to the fused benzene ring.



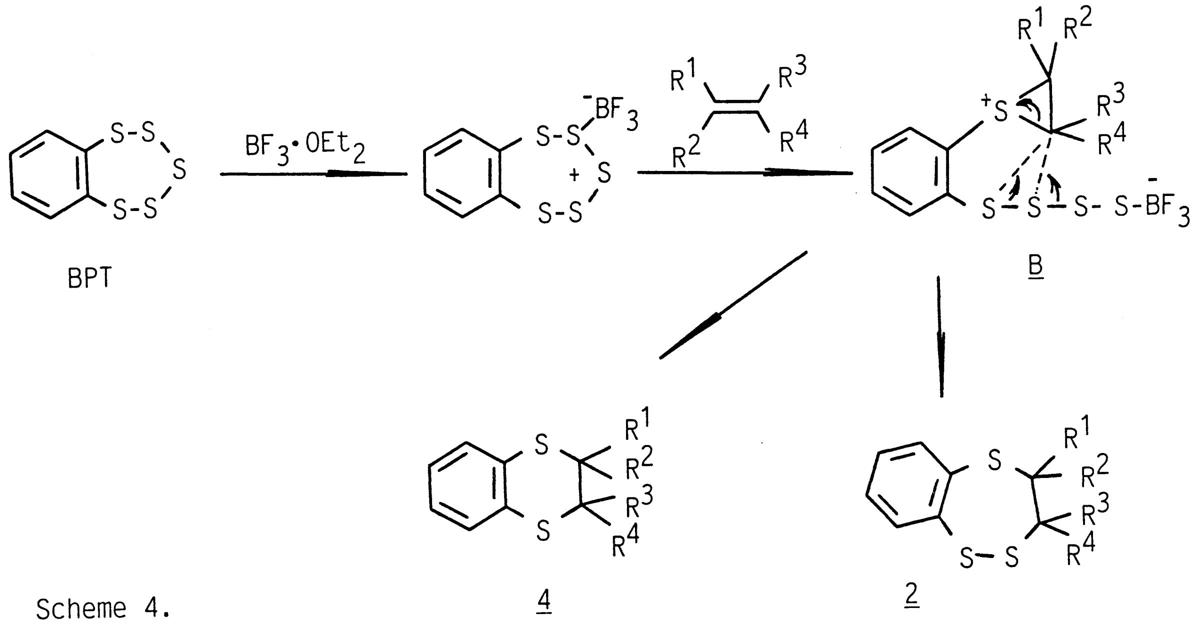
Scheme 2.

A quite different result was obtained in the reaction of 2,3-dimethyl-2-butene 1e with BPT in the presence of $BF_3 \cdot OEt_2$. 1,2,5-Benzotrithiepin was not given in this case but 2,2,3,3-tetramethyl-1,4-benzodithiane(4)[9] was formed in 89% yield along with bis(1,1,2-trimethylpropyl) trisulfide (5, 42%), which corresponds to a very interesting sulfurized product of 1e with BPT (Scheme 3).



Scheme 3.

The whole reaction pathway is rationalized by assuming an episulfonium intermediate B[10] as shown in Scheme 4. Thus, it is conceivable that the steric bulkiness of substituent R^3 or R^4 in the intermediate B would be responsible for the number of sulfur contained in the product. Accordingly, dithiane 4 was formed exclusively in the reaction of 2,3-dimethyl-2-butene.



Scheme 4.

In conclusion, we have developed a new field of organosulfur chemistry in which some interesting 1,2,5-benzotrithiepins are effectively synthesized from BPT. The details on the mechanism and further applications are now under progress in our laboratory.

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9) 4: Oil; IR (KBr) 2960, 1450, 1105, and 740 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 1.48 (s, 12H, CH$_3$ x 4) and 6.85-7.18 (AA'BB', m, 4H, arom); MS (70 eV) m/z 224 (M$^+$). Found: C, 64.24; H, 7.46%. Calcd for $C_{12}H_{16}S_2$: C, 64.24; H, 7.19%.

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