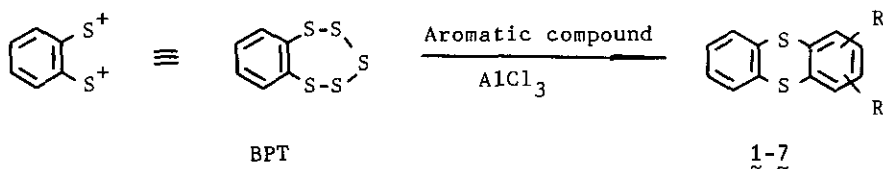


CHEMISTRY ON BENZOPENTATHIEPIN. REACTIONS OF BENZOPENTATHIEPIN WITH AROMATIC COMPOUNDS IN THE PRESENCE OF LEWIS ACID

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Abstract --- Benzopentathiepin (BPT) reacted with many aromatic compounds such as benzene, 1,4-dimethylbenzene, and naphthalene in the presence of Lewis acid to give various thianthrenes in moderate yields. BPT was found to serve as a 1,4-dication synthon.

Recently, much attention has been paid on the chemistry of cyclic polysulfides such as lenthionine and sporidesmin in the viewpoint of biological activity.¹ Especially, current interests have been centered on synthesis and reaction of BPT, which was shown to have acaricidal and fungicidal effects.² We also reported a new synthesis of BPT and related cyclic polysulfides³ and revealed a synthetic utility of BPT as a sulfurization reagent for synthesis of arenethio-sulfonates from corresponding sulfinates.⁴ Based on the reactivity of BPT, we have studied a new synthetic route to heterocycles containing sulfur functional group from BPT. Now we wish to report a novel synthesis of symmetric and various unsymmetric thianthrenes by treating many aromatic compounds with BPT in the presence of Lewis acid such as aluminium chloride. In these reactions, BPT was found to react as a 1,4-dication synthon as shown in Scheme 1.



Scheme 1.

The synthesis of 1,4-dimethylthianthrene (2) was typically carried out as fol-


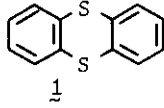
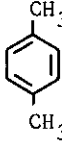
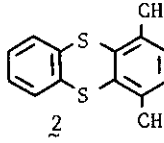
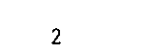
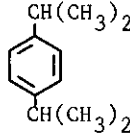
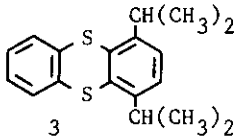
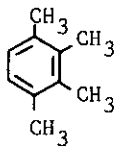
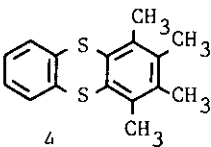
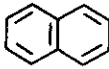
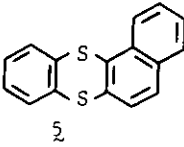
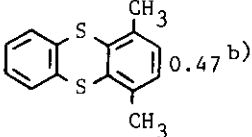
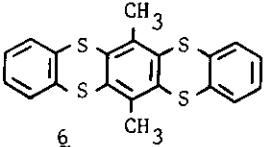
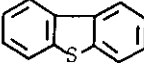
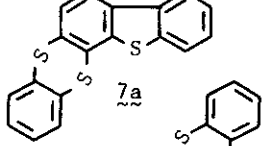
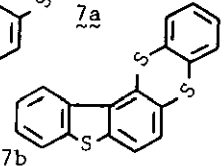
lows. To a solution of BPT (118 mg, 0.5 mmol) in p-xylene (5 ml) was added aluminium chloride (67 mg, 0.5 mmol) and the mixture was stirred at 80 °C for 3 h under nitrogen atmosphere. The reaction was quenched by addition of 5% aq. HCl (7 ml) and ice water (20 ml). The mixture was extracted with benzene (20 ml x 3) and the extracts were washed with 5% aq. NaHCO₃ (30 ml). Chromatography of the residue on aluminium oxide (Woelm, basic) using a mixture of hexane and benzene (v/v, 10/1) gave 1,4-dimethylthianthrene (2, 92 mg, 75%). 2: Colorless crystals; mp 105 °C (from EtOH); ¹H nmr (CDCl₃) δ 2.45 (s, 6H, CH₃ x 2), 7.00 (s, 2H, arom), and 7.13-7.57 (m, 4H, arom); ir (KBr) 2970, 1585, 1450, 1360, 1250, 1115, 1000, 815, and 750 cm⁻¹; ms (70 eV) m/z 244 (M⁺). Anal. Calcd for C₁₄H₁₂S₂: C, 68.81; H, 4.95. Found: C, 68.91; H, 4.99.

As shown in Table 1, benzene and 1,4-dialkylbenzenes readily reacted with BPT in the presence of AlCl₃ to give the corresponding thianthrenes (2-3) in reasonable yields (Table 1). 1,2,3,4-Tetramethylbenzene also reacted with BPT in CH₂Cl₂ to afford exclusively 1,2,3,4-tetramethylthianthrene (4) (Run 4). Interestingly, benzo[a]thianthrene (5) without formation of any isomers was obtained in high yield (93%) upon treating naphthalene (39 mmol) with BPT at 100 °C in the presence of AlCl₃. 5: Colorless crystals, mp 89.5 °C (from EtOH); ¹H nmr (CDCl₃) δ 7.16-7.90 (m, 9H, arom) and 8.36-8.53 (m, 1H, arom); ir (KBr) 3050, 1450, and 740 cm⁻¹; ms (20 eV) m/z 266 (M⁺). Anal. Calcd for C₁₆H₁₀S₂: C, 72.14; H, 3.78. Found: C, 72.39; H, 3.71.

Although the reaction of p-xylene (1 mmol) with excess BPT (2 mmol) afforded only unsymmetrical thianthrene 2 (Run 2), further treatment of isolated 2 (0.47 mmol) with BPT (0.5 mmol) gave a new interesting thianthrene, [1,4]benzodithiino[2,3-b][1,4]dimethylthianthrene 6 (36 mg, 20%) (Run 7). 6: Colorless crystals; mp 291 °C (dec) from EtOH-CHCl₃; ¹H nmr (CDCl₃) δ 2.75 (s, 6H, CH₃ x 2) and 7.17-7.35 and 7.42-7.60 (AA'BB' m, 8H, arom); ir (KBr) 2920, 1450, 1435, 1390, and 740 cm⁻¹; ms (70 eV) m/z 382 (M⁺). Anal. Calcd for C₂₀H₁₄S₂: C, 62.79; H, 3.69. Found: C, 62.75; H, 3.98.

Dibenzothiophene also reacted with BPT to yield two isomers 7a and 7b as shown in Run 8. The structures of 7a and 7b were determined by comparison of ¹H nmr spectra with those of dibenzothiophene in the literature.⁵ 7a: ¹H nmr (CDCl₃) δ 7.21-7.30 (m, 2H), 7.39-7.47 (m, 2H), 7.47-7.54 (m, 1H), 7.51 (d, J 8.1 Hz, 1H), 7.54-7.61 (m, 1H), 7.81-7.87 (m, 1H), 7.94 (d, J 8.1 Hz, 1H), and 8.01-8.07 (m, 1H). 7b: ¹H nmr (CDCl₃) δ 7.22-7.34 (m, 2H), 7.44-7.59 (m, 3H),

Table 1. Synthesis of Various Thianthrenes by Reactions of Aromatic Compounds with BPT in the presence of AlCl₃

Run ^{a)}	Substrate	AlCl ₃		Conditions		Product	Yield ^{c)} mp	
		mmol	mmol	Temp/°C	Time/h		%	°C
1		56	0.5	80	16		44	151 (lit.) ⁶ (157)
2		41	0.5	80	3		75	105
3	1b ^{b)}	1	1	r. t.	32		65	
4		1b ^{b)}	1	r. t.	44		62	83
5		3b ^{b)}	1	r. t.	24		83	170
6		39	0.5	100	5		93	89
7		0.47 ^{b)}	5.5	40	96		20 ^{d)}	291 (dec)
8		3b ^{b)}	1	r. t.	33		43	183
							43	182

a) BPT: 0.5 mmol. b) CH₂Cl₂ (5 ml) was used as a solvent. c) Isolated yield based on BPT. d) Isolated yield based on 1,4-dimethylthianthrene.

7.58 (d, J 8.2 Hz, 1H), 7.64-7.73(m, 1H), 7.72 (d, J 8.2 Hz, 1H), 7.81-7.90 (m, 1H), 9.33-9.42 (m, 1H).

It is noteworthy that unsymmetrical thianthrenes 2-7 were successfully synthesized in satisfactory yields by the present method, since there have been only a few reports on the synthesis of such unsymmetrical thianthrenes.^{7,8} In addition, to our knowledge, the present reaction is the first example of synthetic method for unsymmetrical thianthrenes under acidic conditions. As mentioned above, BPT was found to serve as a 1,4-dication synthon in reactions with active aromatic compounds. Further investigation on applications of BPT to synthesis of heterocycles are now in progress in our laboratory.

REFERENCES

1. K. Morita and S. Kobayashi, Chem. Pharm. Bull., 1967, 15, 988; R. Rahman, S. Safe, and J. Taylor, J. Chem. Soc. C, 1969, 1665. W. Ando, Y. Kumamoto, H. Ishizuka, and N. Tokitoh, Tetrahedron Lett., 1987, 28, 4707; W. Ando, Y. Kumamoto, and N. Tokitoh, Tetrahedron Lett., 1987, 28, 4833; N. Tokitoh, H. Ishizuka, and W. Ando, Chem. Lett., 1988, 657.
2. B. L. Chenard and T. J. Miller, J. Org. Chem., 1984, 49, 1221; B. L. Chenard, R. L. Harlow, A. L. Johnson, and S. A. Vladuchick, J. Am. Chem. Soc., 1985, 107, 3871; J. Nakayama, M. Kashiwagi, R. Yomoda, and M. Hoshino, Nippon Kagaku Kaishi, 1987, 1424.
3. R. Sato, S. Saito, H. Chiba, T. Goto, and M. Saito, Chem. Lett., 1984, 349; R. Sato, S. Saito, H. Chiba, T. Goto, and M. Saito, Bull. Chem. Soc. Jpn., 1988, 61, 1647.
4. R. Sato, Y. Akutsu, T. Goto, and M. Saito, Chem. Lett., 1987, 2161.
5. K. D. Bartle, D. W. Jones, and R. S. Matthews, Tetrahedron, 1971, 27, 5177.
6. P. C. Montevocchi and A. Tundo, J. Org. Chem., 1981, 46, 4998.
7. R. G. Sutherland, A. Piorko, U. S. Gill, and C. C. Lee, J. Heterocycl. Chem., 1982, 19, 801; J. J. Ford, M. R. Willcott III, and K. Smith, J. Heterocycl. Chem., 1982, 19, 1441.
8. A. B. Pierini, M. T. Baumgartner, and R. A. Rossi, J. Org. Chem., 1987, 52, 1089; J. Nakayama, H. Fukushima, R. Hashimoto, and M. Hoshino, J. Chem. Soc., Chem. Commun., 1982, 612.

Received, 2nd August, 1988