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CHEMISTRY ON BENZOPENTATHIEPIN. REACTIONS OF BENZOPENTATHIEPIN WITH ACTIVE METHYLENE COMPOUNDS IN THE PRESENCE OF BASE

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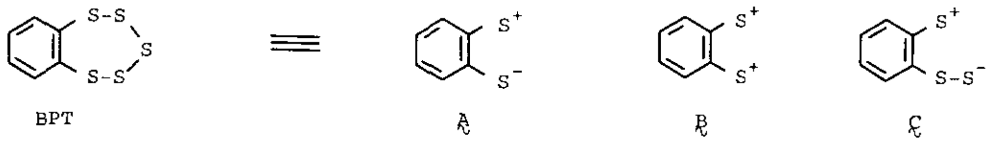
Abstract——Benzopentathiepin (BPT) reacted with various active methylene compounds such as malononitrile, ethyl cyanoacetate, ethyl acetoacetate, acetylacetone, ethyl 2-chloroacetoacetate, and ethyl α-chloropropionate in the presence of base such as triethylamine or sodium ethoxide to give dithiins, dithioles, or 1,2,4-trithiin in satisfactory yields.

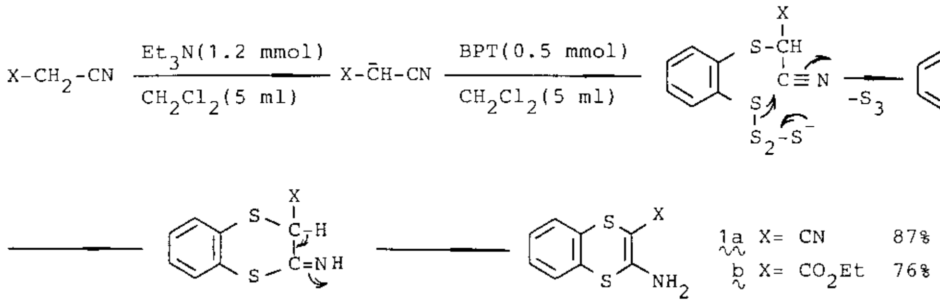
The success of a facile synthesis of BPT,[1] which is a typical cyclic polysulfide and shows a certain fungicidal effect,[2] stimulated some organosulfur chemists to investigate application of BPT as a synthetic reagent.[3] Chenard et al. have reported the formation of 1,4-benzodithiin from BPT and dimethyl acetylenedicarboxylate in the presence of triphenylphosphine.[4] Very recently, we have also revealed the utility of BPT as a sulfurization reagent of alkane- and arenesulfinates converting them to the corresponding thiosulfonates[5] and also as a synthetic reagent of unsymmetrical thianthrenes.[6] Now we wish to report a novel reaction of BPT with various active methylene compounds such as malononitrile, ethyl cyanoacetate, ethyl acetoacetate, acetylacetone, and ethyl α-chloropropionate in the presence of base such as Et_3N or NaOEt to give dithiins **1**, dithioles **2** and **3**, or trithiin **4** in satisfactory yields. In the present reaction, BPT was found to act as synthons **A**, **B**, or **C** as shown in Scheme 1.



BPT **A** **B** **C**

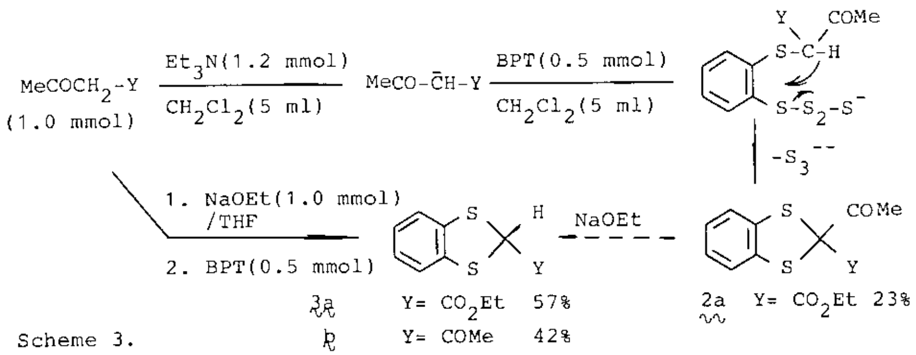
Scheme 1.

The reaction of BPT with active methylene compounds was typically carried out as follows. To a solution of active methylene compound (malononitrile, 1.0 mmol) and Et_3N (1.2 mmol) in CH_2Cl_2 (5 ml) was added dropwise a solution of BPT (0.5 mmol) in CH_2Cl_2 (5 ml) under nitrogen atmosphere and then the mixture was stirred at room temperature for 1 h. After evaporation of CH_2Cl_2 the residue was chromatographed on a column of silica gel using chloroform as an eluent to give 2-amino-3-cyano-1,4-benzodithiin (1a, 179 mg, 87%)(Scheme 2). 1a: Colorless crystals; mp 194 °C (from CH_2Cl_2/hexane, 4/1); ^1H nmr (DMSO-d_6) δ 7.28-7.76 (m, 4H, arom) and 7.82 (s, 2H, NH_2); ir (KBr) 3400, 3280, 3180, 2190, and 1620 cm^{-1}; ms (70 eV) m/z 206 (M^+). Anal. Calcd for $C_9H_6N_2S_2$: C, 52.40; H, 2.93; N, 13.58. Found: C, 52.12; H, 2.77; N, 13.29.



Scheme 2.

Dithiin 1b was also obtained by the reaction of ethyl cyanoacetate with BPT in 76% yield (Scheme 2). These results suggest apparently that BPT serves as a 1,4-dipole synthon A to afford dithiin 1. Although ethyl acetoacetate was found to react with BPT in the presence of Et_3N to give 2-acetyl-2-ethoxycarbonyl-1,3-

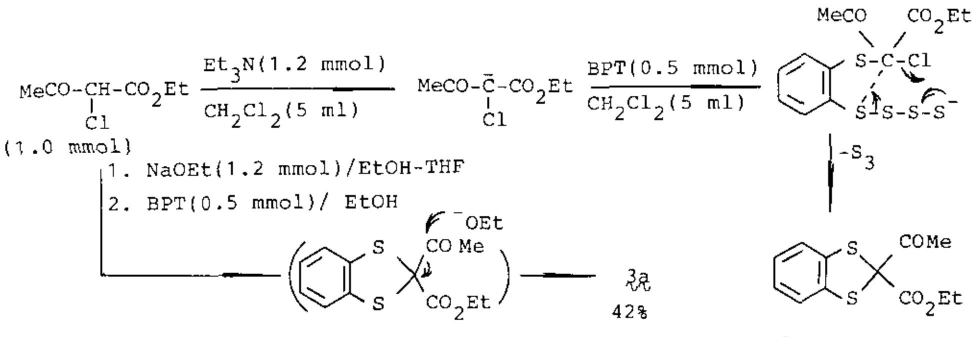


Scheme 3.

benzodithiole (2a), 2-ethoxycarbonyl-1,3-benzodithiole (3a) was formed in 57% yield in the presence of NaOEt in EtOH-THF. Acetylacetone gave similarly 2-acetyl-1,3-benzodithiole (3b) (Scheme 3). Since the dithiole 2a was found to react with NaOEt to afford 3a[7], 3a and 3b seem to be formed by the nucleophilic attack of ethoxide on acetyl carbonyl group in 2 followed by protonation. In these reactions, BPT was shown apparently to serve as a 1,4-dication synthon B.

2a: Oil; ^{1}H nmr ($CDCl_3$) δ 1.30 (t, J 7.0 Hz, 3H, $-CH_2C\underline{H}_3$), 2.41 (s, 3H, $-C\underline{H}_3$), 4.32 (q, J 7.0 Hz, $-C\underline{H}_2CH_3$), and 6.96-7.30 (m, 4H, arom); ir (neat) 1730 and 1710 cm^{-1}; ms (70 eV) m/z 268 (M^+). Anal. Calcd for $C_{12}H_{12}O_3S_2$: C, 53.71; H, 4.51. Found: C, 53.91; H, 4.55. 3a: Colorless crystals; mp 41.0° C (from hexane); ^{1}H nmr ($CDCl_3$) δ 1.25 (t, J 7.0 Hz, 3H, $-CH_2C\underline{H}_3$), 4.20 (q, J 7.0 Hz, 2H, $-C\underline{H}_2CH_3$), 5.23 (s, 1H, $-C\underline{H}<$), and 6.95-7.26 (m, 4H, arom); ir (KBr) 1753 cm^{-1}; ms (70 eV) m/z 226 (M^+). Anal. Calcd for $C_{10}H_{10}O_2S_2$: C, 53.07; H, 4.45. Found: C, 53.12; H, 4.45.

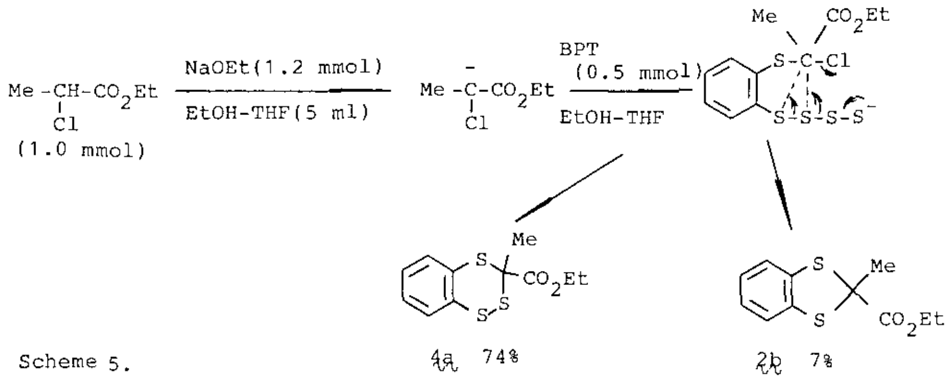
1,3-Dithioles 2a and 3a were also obtained upon treating ethyl 2-chloroacetoacetate with BPT in the presence of base as shown in Scheme 4. These results suggest that BPT functions as a 1,4-dipole synthon A.



Scheme 4.

An interesting result was obtained by the reaction of ethyl α-chloropropionate with BPT in the presence of NaOEt in THF; 3-ethoxycarbonyl-3-methyl-1,2,4-benzotrithiin (4a) was given in 74% yield together with 1,3-dithiole 2b as shown in Scheme 5. This result indicates that BPT serves as a 1,5-dipole synthon C.[8]

4a: Oil; ^{1}H nmr ($CDCl_3$) α 1.25 (t, J 7.0 Hz, 3H, $-CH_2-C\underline{H}_3$), 2.06 (s, 3H, $-CH_3$), 4.24 (q, J 7.0 Hz, 2H, $-C\underline{H}_2CH_3$), and 7.00-7.73 (m, 4H, arom); ir (neat) 1730 cm^{-1}; ms (70 eV) m/z 272 (M^+). Anal. Calcd for $C_{11}H_{12}O_2S_3$: C, 48.50; H, 4.44.



Scheme 5.

Found: C, 48.40; H, 4.46.

Further investigation on synthetic versatility of BPT in the new field of cyclic polysulfides[9] is now under progress in our laboratory.

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