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Benzopentathiepin as Sulfurization Reagent. Novel Synthesis of Thiosulfonates from Sulfinates

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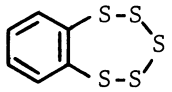
Sodium alkane- and arenesulfinates were readily sulfurized with benzopentathiepin in usual organic solvents at room temperature to give corresponding thiosulfonates in good yields.

Much attention of organosulfur chemists has recently been focused on the synthesis and chemistry of sulfur-linked compounds such as benzopentathiepin (BPT) which have some interesting chemical and physical properties.[1] There has been, however, only a few reports on the reaction of BPT with organic compounds.[2] Our success of the efficient synthesis of BPT[3] prompted us to study on its chemical properties, for example, the reactivities of BPT as a sulfurization reagent. Now we wish to report the first successful example of the sulfurization with BPT, which converts sodium alkane- and arenesulfinates to the corresponding synthetically and biologically important sodium alkane- and arenethiosulfonates in good yields(Eq. 1).[4]

$$\underset{\underline{1a\text{-}j}}{R\text{-}SO_2Na} \xrightarrow{BPT} \underset{\underline{2a\text{-}j}}{R\text{-}SO_2SNa} \qquad (1)$$



BPT

A typical procedure is as follows. To a solution of sodium 2-(ethoxycarbonyl)-ethanesulfinate(1i, 0.5 mmol)[5] in methanol-chloroform(1/1, v/v) (10 ml) was added BPT(0.5 mmol), and then the mixture was stirred at room temperature for 5 min. After the reaction was complete, the solvent was evaporated and the residue was washed with chloroform(10 ml) and extracted with methanol. The residue obtained by evaporation of methanol was again extracted with ethanol(10 ml). Evaporation of ethanol gave colorless crystals, 2i. Compound 2i: IR(KBr) 1070, 1170, 1290, and 1700 cm^{-1}; ^{1}H-NMR (D_2O) 1.27 (3H, t, 7Hz, CH_3), 2.93(2H, t, 7Hz, $-CH_2-$), 3.58(2H, t, 7Hz, $-CH_2-$), and 4.19(2H, q, 7Hz, $-CH_2-$); Found: C, 27.35; H, 4.24%. Calcd for $C_5H_9O_4S_2Na$: C, 27.27; H, 4.12%.

The results were summarized in Table 1. The generality of the present reaction was also illustrated in runs 6-14. A thiosulfonate was obtained in a good yield even when only 0.5 equiv. of BPT was used as shown in run 4, suggesting that BPT as a sulfurization reagent could give two sulfur atoms to sulfinate. It is noteworthy that the reaction is compatible with reactive car-

Table 1. Synthesis of thiosulfonates(2a-j) from sulfinates(1a-j) with BPT

Run[a]	Substrate R-SO_2Na/R		BPT (mmol)	Solvent (v/v)	React. time/h	Yield/%		Mp (lit.) °C
1	C_6H_5-	1a	0.5	$CHCl_3$/MeOH(1/1)	5	94	2a	287(287)dec.[7]
2			0.5	CH_2Cl_2/MeOH(1/1)	5	98	2a	
3			0.5	Benzene/MeOH(1/1)	5	99	2a	
4			0.25	$CHCl_3$/MeOH(1/1)	10	90	2a	
5			0.16	Benzene/MeOH(1/1)	8	65	2a	
6	4-CH_3-C_6H_4-	1b	0.5	Benzene/MeOH(1/1)	5	100	2b	290(290)dec.[7]
7	4-CH_3O-C_6H_4-	1c	0.5	Benzene/MeOH(1/1)	3	96	2c	243 dec.
8	4-Cl-C_6H_4-	1d	0.5	Benzene/MeOH(1/1)	10	82	2d	268(268)dec.[7]
9	4-Br-C_6H_4-	1e	0.5	Benzene/MeOH(1/1)	11	85	2e	235 dec.
10	CH_3-	1f[5]	0.5	$CHCl_3$/MeOH(1/1)	5(min)	78	2f[8]	226 dec.
11	C_6H_5-CH_2-	1g[5]	0.5	$CHCl_3$/MeOH(1/1)	5(min)	81	2g	225 dec.
12	C_6H_5-CH_2CH_2-	1h[5]	0.5	$CHCl_3$/MeOH(1/1)	5(min)	86	2h	255 dec.
13	EtOCOCH_2CH_2-	1i[5]	0.5	$CHCl_3$/MeOH(1/1)	5(min)	69	2i	166
14	Cl-$(CH_2)_4$-	1j[5]	0.5	$CHCl_3$/MeOH(1/1)	5(min)	78	2j[8]	129

a) Substrate: 0.5 mmol, room temperature.

boethoxyl and chloro groups(runs 13 and 14), since the thiosulfonates, 2i and and 2j, have never been obtained by the known method.[6,7] Thus, we could confirm a synthetic utility of BPT as a sulfurization reagent and add a novel procedure for synthesis of sodium alkane- and arenethiosulfonates to the known procedures. This method has some advantages, i.e., good yields and experimental convenience. In all the reactions BPT was converted to unidentified polymer. The mechanism of this reaction and further synthetic applications of BPT are now under investigation.

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8) Compounds 2f and 2j were isolated and characterized as $CH_3SO_2SNa \cdot H_2O$ and Cl-$(CH_2)_4$-$SO_2SNa \cdot H_2O$ respectively.

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