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REACTION OF SULFENAMIDES WITH DI-ALKYL AND TRIALKYL PHOSPHITES. AN EFFICIENT SYNTHESIS OF PHOSPHORAMIDATES BY UNUSUAL SUBSTITUTION AT S-N BOND IN (2-BENZOTHIAZOLYL)SULFENAMIDES

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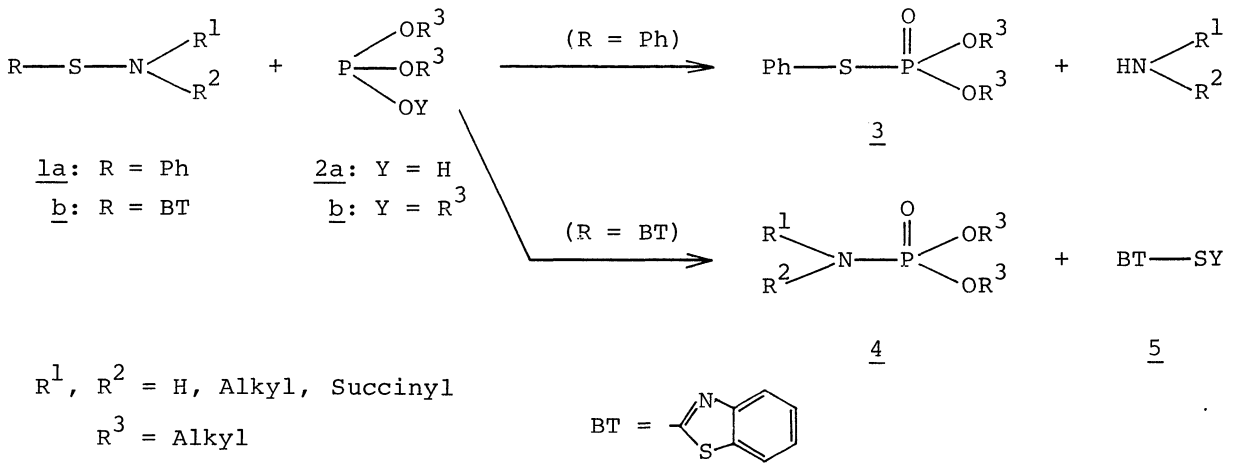
Regioselective attack of the trivalent phosphorus atom of dialkyl and trialkyl phosphites on either nitrogen or sulfur atom of sulfenamides has been found. The reaction of phenylsulfenamides with dialkyl phosphites yielded phosphorothiolates, whereas the treatment of (2-benzothiazolyl)sulfenamides with dialkyl and trialkyl phosphites gave phosphoramidates in excellent yields.

In the preceding papers, we reported an efficient electrosynthesis of sulfenamides 1 by either direct or NaBr-promoted cross-coupling reaction of amines and disulfides.[1] Our attention has, in turn, been focused on the versatile use of sulfenamides 1 as a reagent for making hetero-hetero atom bond.[2]

We wish to report here convenient N-P and S-P bond making reactions by regioselective attack of dialkyl and trialkyl phosphites 2 onto either sulfur or nitrogen atom of sulfenamides 1, leading to phosphorothiolates 3[3] and phosphoramidates 4[4], respectively.

Scheme 1



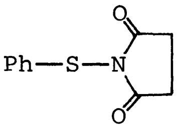
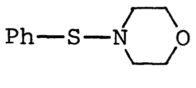
Reaction of sulfenamide 1a (R = Ph; R^1, R^2 = succinyl) with slightly excess dialkyl phosphites 2a (1.05-1.1 equiv.) in benzene under stirring at room temperature (20 h) afforded 89-90% yields of phosphorothiolates 3 (Table I, entries 1-3). Sulfenamides 1a (R = Ph; R^1, R^2 = $-CH_2CH_2-O-CH_2CH_2-$) also reacted with 2a to give 3 (67-96%) along with phosphoramidates 4 (trace) (entries 4-6). Dramatical change on the products was encountered in the reaction of (2-benzothiazolyl)sulfenamides 1b (R = BT; R^1, R^2 = H, alkyl) with 2a, leading to the exclusive formation of 4 (Table II), indicating that the nucleophilic attack of 2a occurs on the nitrogen atom of the S-N bond of 1b.

The bond polarization derived from differences in electronegativity between sulfur and nitrogen seems to cause regioselective nucleophilic attack on the electron-defficient sulfur atom of the S-N bond, permitting the displacement of the amino group with various nucleophiles.[2] The unusual cleavage of the S-N bond of 1b (R = BT) can be explained by assuming that the powerful electron-withdrawing effect of 2-benzothiazolyl moiety (BT) would give rise to inversion of the polarization of the S-N bond by donating electron from nitrogen to sulfur atom through (d-p) pai bond.[5]

The reaction of 1b with 2a gave 4 together with 5 (Y = H) in good yields except for 1b bearing t-butyl or dibutylamino moiety (Table II, entries 5, 6, 14, 15, 23, and 24). It can be reasonably understood by assuming that the nucleophilic attack of 2a on the nitrogen atom of 1b is effectively inhibited by the bulky alkyl group attached to the nitrogen atom of 1a.

The unexpected behavior of 1b led us to explore an additional route to 4 from trialkyl phosphites 2b. Some results are listed in Table III.
The reaction would proceed through nucleophilic attack of 2b onto sulfur atom of 1b, affording phosphonium ion 6 (Scheme 2). Subsequent attack of thiolate ion 7 at α-position of alkyl group (R^3) of 6 would give 4 together with alkyl sulfides 5 (Y = R^3).

Table I Reaction of Phenylsulfenamides with Dialkyl Phosphites

Entry	Sulfenamide 1a	$(R^3O)_2POH$ 2a R^3	Product,[a] Yield %[b] $(R^3O)_2P(O)SPh$ 3	 $(R^3O)_2P(O)NR^1R^2$ 4
1		Methyl	89	—
2		Ethyl	99	—
3		Isopropyl	96	—
4		Methyl	67	trace
5		Ethyl	83	5
6		Isopropyl	96	trace

a) Identical in all respects with the authentic samples (ref. 3a and 4).
b) Isolated yields.

Table II Reaction of (2-Benzothiazolyl)sulfenamides with Dialkyl Phosphites

Entry	Phosphite $\underline{2a}$	Sulfenamide $\underline{1b}$		Product, Yield %[a)]		
	$(R^3O)_2POH$	$BTS—NR^1R^2$		$(R^3O)_2P(O)NR^1R^2$	$(R^3O)_2P(O)SBT$	BTSH[b)]
	R^3	R^1,	R^2	$\underline{4}$	$\underline{3}$	($BTSR^3$)
1	Methyl	Propyl	H	80	—	95 (5)
2	"	Benzyl	H	82	—	100
3	"	$-CH_2CH_2OCH_2CH_2-$		81	—	98
4	"	$-(CH_2)_5-$		93	—	93 (7)
5	"	$\underline{t}$-Butyl	H	21	—	36 (64)
6	"	Butyl	Butyl	28	—	44 (52)
7	Ethyl	Propyl	H	94	—	99
8	"	Benzyl	H	80	—	100
9	"	Cyclohexyl	H	83	—	100
10	"	Isopropyl	H	91	—	100
11	"	$-CH_2CH_2OCH_2CH_2-$		98	—	96
12	"	$-(CH_2)_5-$		93	—	100
13	"	Ethyl	Ethyl	80	—	100
14	"	$\underline{t}$-Butyl	H	52	18	41
15	"	Butyl	Butyl	60	—	98
16	Isopropyl	Propyl	H	91	8	90
17	"	Benzyl	H	90	—	100
18	"	Cyclohexyl	H	87	—	100
19	"	Isopropyl	H	72	17	100
20	"	$-CH_2CH_2OCH_2CH_2-$		96	—	100
21	"	$-(CH_2)_5-$		82	trace	100
22	"	Ethyl	Ethyl	89	trace	93
23	"	$\underline{t}$-Butyl	H	trace	26	70
24	"	Butyl	Butyl	trace	45	50

a) Isolated yields; their IR and ^1H NMR spectra were identical with those of authentic samples (ref. 3a and 4). b) Recovered $\underline{5}$ (Y = H) can be used for preparation of sulfenamides $\underline{1b}$ by electrolysis procedure (ref. 1a).

Scheme 2

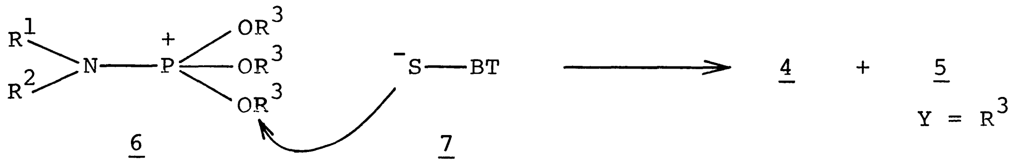
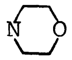


Table III Reaction of N, N-Oxydiethylene-(2-benzothiazolyl)sulfenamide with Trialkyl Phosphites

Entry	$(R^3O)_3P$ 2b	Product, Yield %[a]		
	R^3	$(R^3O)_2P(O)$  4	$BTSR^3$	(BTSH) 5
1	Methyl	91	83	(17)
2	Ethyl	74	70	(30)
3	Isopropyl	84	72	(28)
4	Butyl	85	76	(21)

a) Isolated yields; all products indicated satisfactory IR and ^1H NMR spectra.

References and Notes

1) (a) S. Torii, H. Tanaka, and M. Ukida, J. Org. Chem., 43, 3223 (1978); (b) idem., ibid., 44, 1554 (1979).

2) Sulfenamides 1 have been used in making hetero-hetero atom bonds: S-S bond, (a) D. N. Harpp and T. G. Back, J. Org. Chem., 36, 3828 (1971); (b) D. N. Harpp, D. K. Ash, T. G. Back, J. G. Gleason, B. A. Orwing, and W. F. VanHorn, Tetrahedron Lett., 1970, 3551; (c) K. S. Boustany and A. B. Sullivan, ibid., 1970, 3547. S-N bond, (d) D. N. Harpp and T. G. Back, ibid., 1971, 4953; (e) D. A. Armitage, M. J. Clark, and A. M. White, J. Chem. Soc., C, 3141 (1971). S-P bond, (f) K. A. Petrov, N. K. Bliznyuk, and V. A. Savostenok, Zh. Obshch. Khim., 31, 1361 (1961); Chem. Abstr., 55, 23317 (1961). Displacement of the sulfenyl moiety of the sulfenamides 1 with nucleophiles has not appeared yet.

3) Homologues of 3 are of interest as potential pesticides and variety of synthetic methods have been reported: (a) S. Torii, H. Tanaka, and N. Sayo, J. Org. Chem., 44, 2938 (1979); (b) A. Zwierzak, Synthesis, 1975, 507, and references cited therein.

4) A series of phosphoramidates 4 have attracted much attention as effective insecticides and many efforts have been made to explore an efficient synthetic procedure: S. Torii, N. Sayo, and H. Tanaka, Tetrahedron Lett., 1979, 4471 and references cited therein.

5) F. A. Davis, Int. J. Sulfur Chem., 8, 71 (1973).

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