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REACTIONS OF BENZOTHIETE WITH PHOSPHORUS NUCLEOPHILES
- A NOVEL TYPE OF ARBUZOV REARRANGEMENT

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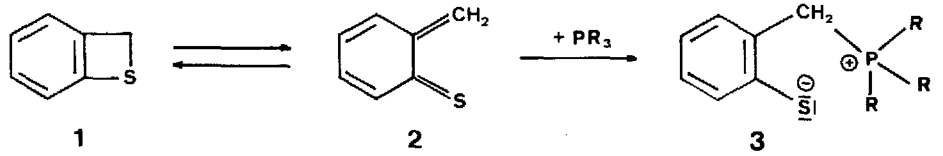
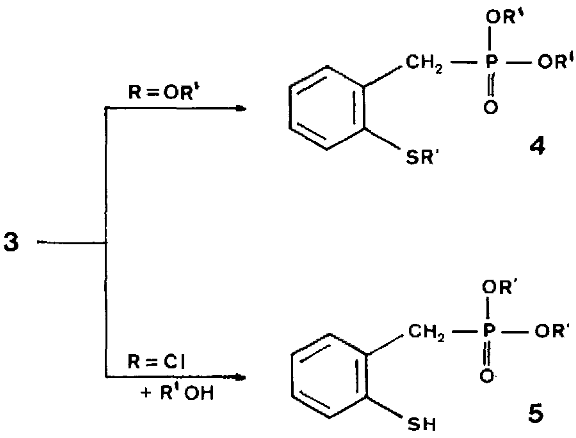
Abstract: The reaction of trialkylphosphites or related P-nucleophiles with benzothiete (1) leads to zwitter ionic species, which show an Arbuzov - like rearrangement to the products 4 and 7, respectively. New heterocyclic ring systems are generated in the case of cyclic esters. The normal S_N2 reaction leads to the 1:2 adducts 9, whereas in an S_N1 process the 1:1 adduct 13 is formed.

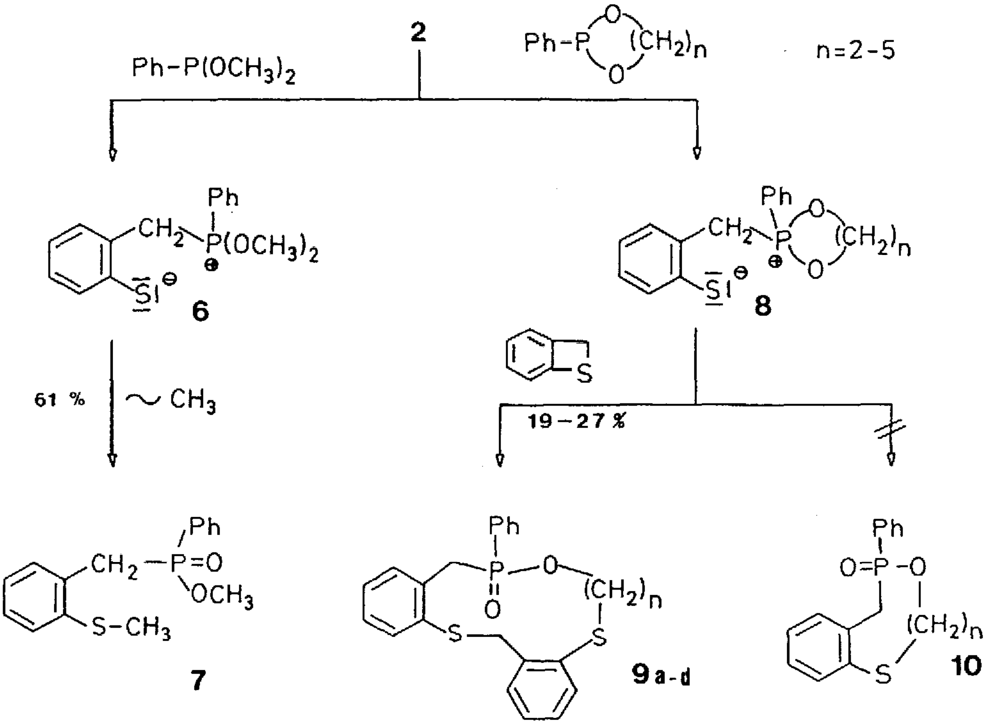
Benzothiete (1) is an extremely useful auxiliary for the synthesis of many sulfur containing heterocyclic ring systems$^{1)}$. The o-quinoidal form 2 possesses a relative high-lying HOMO (- 8.96 eV) and a very low-lying LUMO (- 1.64 eV)$^{2)}$. The latter provokes a high reactivity towards nucleophiles. In boiling toluene the four-membered ring of 1 is opened and trialkylphosphites can be added at the exocyclic carbon center leading to the zwitter ionic structure 3 (R = OCH_3, OC_2H_5). Instead of a ring closure reaction in the following step a rearrangement





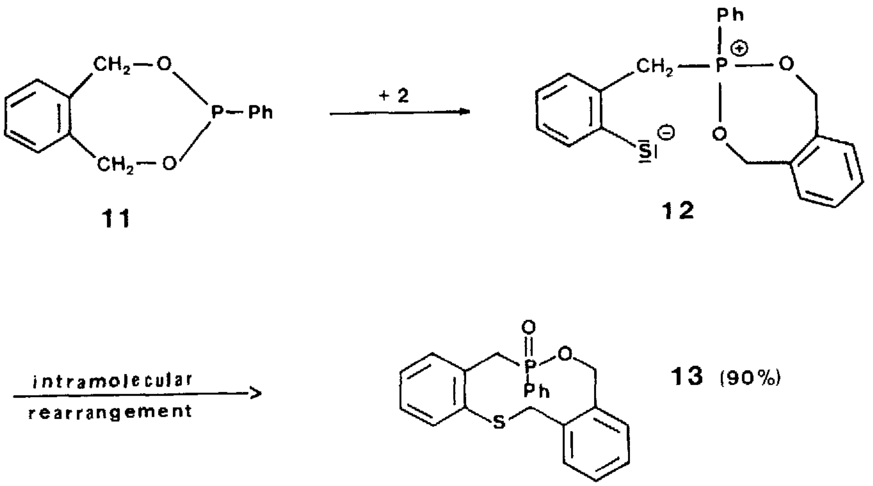
R'	a OCH_3	b OC_2H_5
4	72 %	70 %
5	38 %	39 %

occurs by migration of an alkyl group[3)] to the sulfur atom bearing a negative charge. Thus the phosphonates 4a,b are generated. The formation of the energy rich P=O double bond is certainly the driving force for this process - a fact which directly reminds on the Arbuzov rearrangement[4,5)]. The attack on the sulfur atom can be avoided if PCl_3 is used and the zwitter ion 3 (R = Cl) is scavenged by methanol or ethanol. Under these conditions the phosphonates 5a,b can be obtained.



Besides trialkylphosphites phenylphosphinic acid dialkyl esters can be applied ($2 \rightarrow 6 \rightarrow 7$). Cyclic esters of phenylphosphinic acid should lead to heterocyclic ring system containing phosphorus, oxygen, and sulfur. However, in our original experiments never a 1:1 adduct was gained ($2 \rightarrow 8 \nrightarrow 10$). It turned out that the rearrangement of the intermediate 8 always requires a second molecule benzothiete; thus the macrocyclic systems 9a-d (n = 2, 3, 4, 5) are formed in a 1:2 addition. Obviously, the steric demands for an S_N2-transition state are to high, so that an intramolecular rearrangement doesn't occur - even not when a diluted solution of benzothiete and an excess amount of cyclic ester are used.

The only chance for an intramolecular process and the formation of a 1:1 adduct should be given by a mechanistic change from S_N2 to S_N1. Indeed, this assumption can be verified by the reaction of the benzylic system 11 which furnishes in a yield of 90% the 1,6,2-oxathiaphosphecine ring 13.



The products 4a,b, 5a,b, 7, 9a-d, and 13[6)] are colourless liquids which can be purified by column chromatography on silica gel with acetic acid ethyl ester. The ^{1}H- and ^{13}C-chemical shifts for the phosphonates 4, 5 and for 7 are listed in table 1.

Table 1. ^{1}H- and ^{13}C-NMR Data of 4a,b, 5a,b and 7 (δ-Values in $CDCl_3$)

Compound	P-CH$_2$	S····C·······C		O — C·······C		aryl
4a	3.40	2.47		3.64		7.13 - 7.33 (4H)
	30.2	17.0		52.6		125.6 - 138.1 (6C)
5a	3.37	3.97		3.67		7.12 - 7.40 (4H)
	31.8	--		52.9		127.0 - 132.9 (6C)
7	3.52/3.56	2.26		3.58		7.04 - 7.61 (9H)
	35.1	17.4		51.4		125.7 - 138.3 (12C)
4b	3.38	2.86	1.20	3.99	1.22	7.11 - 7.40 (4H)
	31.2	28.9	14.3	62.0	16.3	126.4 - 136.2 (6C)
5b	3.36	4.07		4.01	1.23	7.11 - 7.40 (4H)
	32.7	--		62.3	16.3	126.8 - 132.8 (6C)

The products 9a-d and 13 represent novel types of medium or large heterocyclic ring systems. The most important NMR data are summarized in table 2.

Table 2. ^{1}H- and ^{13}C-NMR Data of 9a-d and 13 (δ-Values in $CDCl_3$)

Compound	P-CH_2	S-CH_2	O— $(CH_2)_n$·········S	aryl
9a	3.47/3.67	4.38/4.74	4.07/4.33, 2.96/3.06	6.67 - 7.57
(n=2)	36.1	38.4	62.8 38.8	126.9 - 140.7
9b	3.29/3.62	4.50/4.56	3.89/4.18, 1.80, 3.00	7.08 - 7.73
(n=3)	35.8	37.8	62.5 29.4 33.3	126.4 - 139.9
9c	3.15/3.44	4.34/4.49	3.66/4.10, 1.87, 1.67, 2.93/3.07	6.95 - 7.67
(n=4)	35.6	37.4	64.4 28.9 26.3 36.6	125.4 - 139.0
9d	3.38/3.46	4.21/4.23	3.65/3.99, 1.71/1.88, 1.53, 1.62, 3.05/3.12	6.96 - 7.65
(n=5)	35.6	37.7	64.1 29.6 24.0 27.3 34.5	125.9 - 137.4
13	3.72	3.40	4.66/4.93 (OCH_2)	6.85 - 7.53
	35.4	37.1	63.5	127.3 - 135.6

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References and Notes

1) D. Jacob, H.-P. Niedermann and H. Meier, Tetrahedron Lett. 27, 5703 (1986) and references cited therein.
2) H. Meier, H.-L. Eckes, H.-P. Niedermann and H. Kolshorn, Angew. Chem. 99, 1040 (1987); Angew. Chem. Int. Ed. Engl. 26, 1046 (1987).
3) Aryl groups are under these conditions not capable of a cationic migration. In the presence of triarylphosphites the reaction stops at the zwitter ionic species 3.
4) B.A. Arbusow, Pure Appl. Chem. 9, 307 (1964).
5) Compare also the reaction of trialkylphosphites with acrolein: G. Kamai and V.A. Kukhtin, Dokl. Akad. Nauk SSSR 112, 868 (1957); Chem. Abstr. 51, 13742f (1957).
6) The reactions were performed in boiling toluene. A solution of 5 mmol (0.61g) 1 was added dropwise to a solution of 20 mmol P-nucleophile and refluxed for several hours, until no more starting material 1 can be detected by TLC.

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