

Das Reagenz • The Reagent

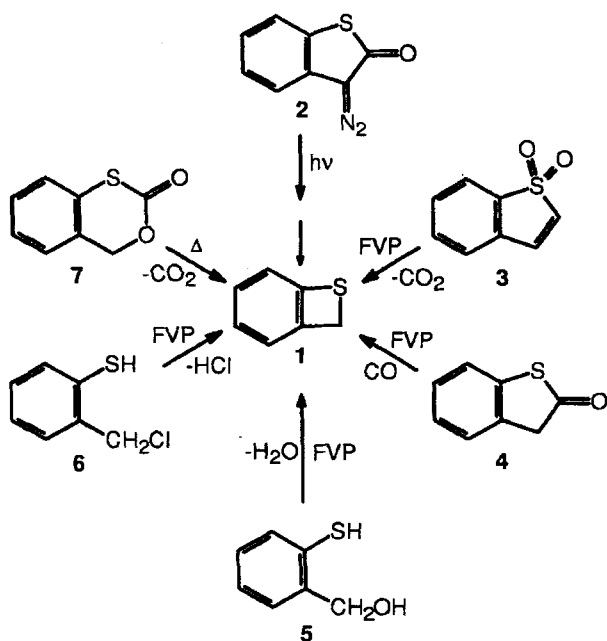
Benzothiete, a Versatile Reagent in Heterocyclic Syntheses

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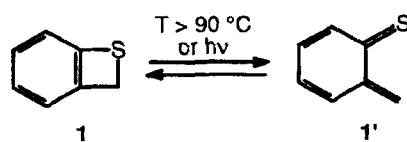
2*H*-Benzo[*b*]thiete (1) and some of its derivatives were first prepared by a photochemical ring contraction of 3-diazo-benzo[*b*]thiophen-2(3*H*)-one (2) and subsequent degradation steps [1]. This process as well as a related ring contraction, in which the Wolff rearrangement was substituted by the Favorsky rearrangement [2], are somewhat laborious and therefore the flash vacuum pyrolyses (FVP) by extrusion of CO₂ from sulfone 3 [3], CO from thiolactone 4 [4], H₂O from thiophenol 5 [5], and HCl from thiophenol 6 [6, 7] were a great preparative improvement. Very recently we found with the thiocarbonate 7 another precursor, which can be applied in normal thermolysis reactions in solution [8]. Since FVP techniques have always a strictly limited turnover per hour, this is again a decisive step forward in order to use benzothiete (1) in a large preparative scale.



Scheme 1

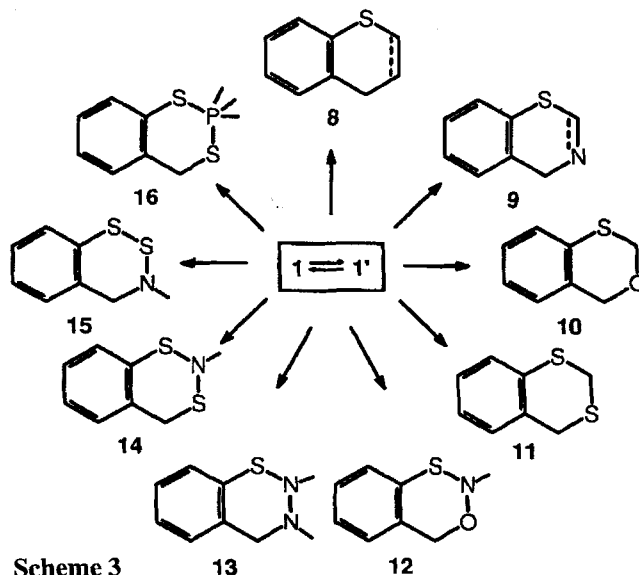
Due to the facile thermal or photochemical opening of the 4-membered ring, 2*H*-benzo[*b*]thiete (1) is extremely reactive.

The relatively high lying HOMO and the low lying LUMO of the *o*-thiobenzoquinonemethide (1') permit the attack of electrophilic as well as nucleophilic reagents [9, 10].



Scheme 2

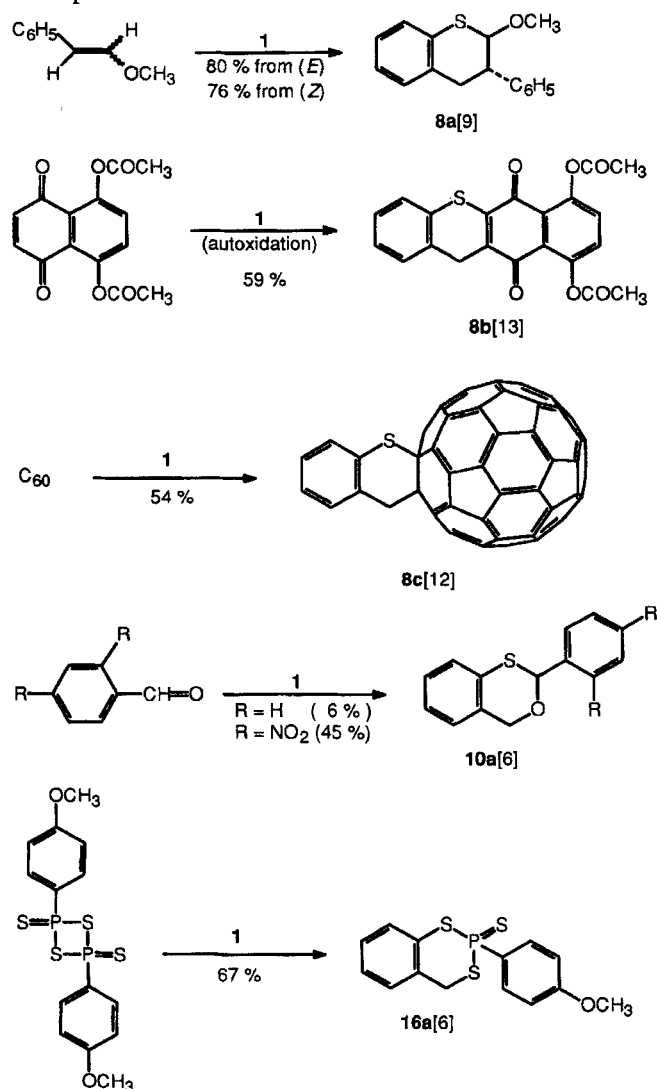
Thus 1 proved to be a very versatile synthon for the preparation of 5-, 6-, 7-, 8-, 9-, 10-membered and macrocyclic ring compounds containing sulfur and possibly further hetero atoms [6]. Most obvious is the cycloaddition of the 8π system 1' with 2π components having CC, CN, CO, CS, NO, NN, NS, PS double bonds or CC or CN triple bonds. Scheme 3 provides a survey over these [8π + 2π] cycloaddition reactions. The *regioselectivity* can often be predicted by the FMO theory, although the reactions are not necessarily concerted as the stereochemical issue reveals [9].



Scheme 3

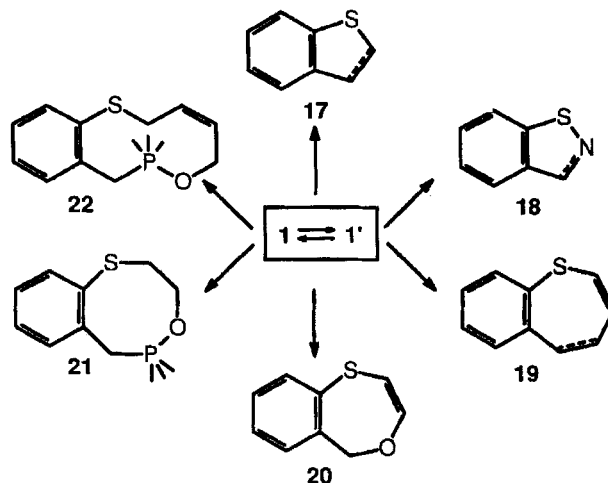
The reaction of $1 \rightleftharpoons 1'$ with electron-rich or electron-deficient olefins leads to *3,4-dihydro-2H-1-benzothiopyrans* (**8**) [5,6,9,11-13], alkynes yield *4H-1-benzothiopyrans* (**8**) [6,11]. *3,4-Dihydro-2H-1,3-benzothiazines* (**9**) are formed in the reaction with imines, oximes, and carbodiimides [14-17]; correspondingly *4H-1,3-benzothiazines* (**9**) are obtained from electron-deficient nitriles [18]. Aldehydes and ketones with electron withdrawing groups furnish *4H-3,1-benzoxathiins* (**10**) [6,19]. Similar $[8\pi + 2\pi]$ cycloaddition reactions lead to *4H-1,3-benzodithiins* (**11**) [6,18], *4H-3,1,2-benzoxathiazines* (**12**) [20], *3,4-dihydro-2H-1,2,3-benzothiadiazines* (**13**) [6], *4H-1,3,2-benzodithiazines* (**14**) [6], *4H-1,2,3-benzodithiazines* (**15**) [16] and *4H-1,3,2-benzodithiaphosphorins* (**16**) [6]. A few selected examples are summarized below.

Examples to Scheme 3:



Besides 6-membered ring systems many other heterocycles are accessible on the basis of *2H-benzo*[*b*]thiethene (**1**).

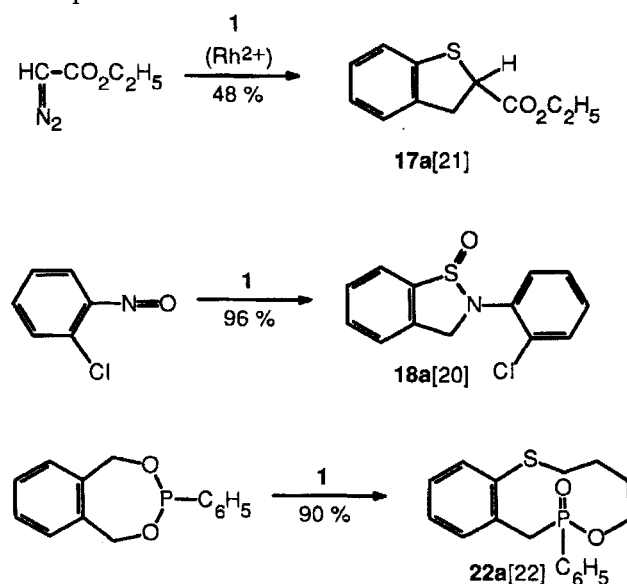
2,3-Dihydrobenzo[*b*]thiophenes and *benzo*[*b*]thiophenes (**17**) are obtained in the reaction of **1** and diazo compounds (and subsequent oxidation) [21] or by cycloaddition of **1** and vinylene carbonate and a consecutive rearrangement [6].



Scheme 4

Derivatives of *1,2-benzothiazol* (**18**) are generated by the reaction of **1** and nitroso compounds or primary amines. In the first case a rearrangement is involved, in the second case an oxidation process [6]. Rh^{2+} -stabilized carbenoids generated from α,β -unsaturated diazo compounds can lead to *4,5-dihydro-1-benzothiepins* (**19**) [21]. A *1-benzothiepin* (**19**) is obtained in the reaction of **1** and perhalogenated cyclopropene [6]. Further 7-membered ring compounds, namely *5H-4,1-benzoxathiepins* (**20**) can be isolated from diazo ketones and **1** in the presence of rhodium acetate. Certain P-nucleophiles can enlarge the 4-membered thiete ring to 8- and 10-membered rings, to derivatives of *4,1,5-benzoxathiaphosphocine* (**21**) and *6,1,7-benzoxathiaphosphocine* (**22**) [6, 22]. Some selected examples are compiled below.

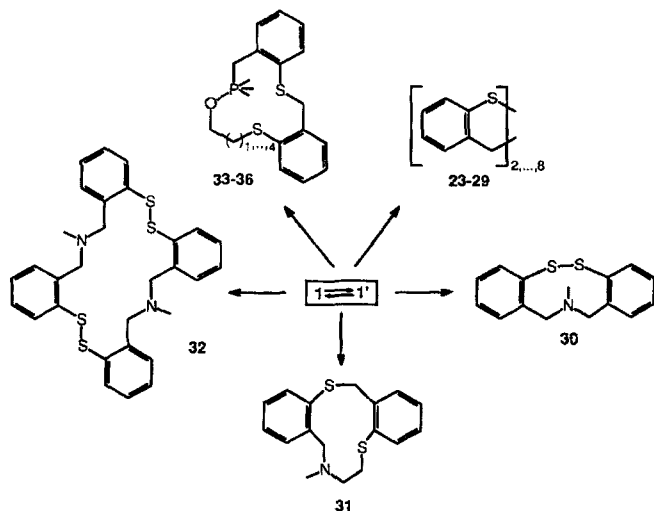
Examples to Scheme 4:



The heterocyclic classes of compounds **8**–**22** are all obtained in 1:1 addition processes of *2H-benzo*[*b*]thiethene (**1**) and the respective reaction partner. Cyclodimerization and cyclo-oligomerization reactions of **1** generating *6H,12H-dibenzo*[*b,f*][*1,5*]dithiocine (**23**) and the thiocrown ethers **24**–**29** are

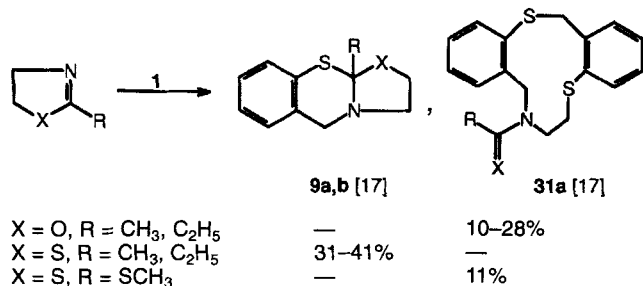
always competitive processes; thus, low yields of **8–22** are accompanied by high yields of **23–29**.

Additionally, there is a series of 2:1 reactions. Scheme 5 shows the formation of heterocycles in which two benzothiete moieties are incorporated [6, 17, 22]. Moreover, 1:2 adducts can be observed in some cases, i.e. the primary cycloadduct of **1**, adds another reaction partner yielding polycyclic heterocycles [6].



Scheme 5

Examples to Scheme 5 (and 3):



Finally, it should be pointed out that the three isomeric naphthothietes [23] and benzo[1,2-b:4,5-b']bisthiete [24] can undergo reactions similar to those observed for **1** [23]. Especially the latter compound is a very useful reagent for the generation of band-shaped systems by repetitive cycloadditions.

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