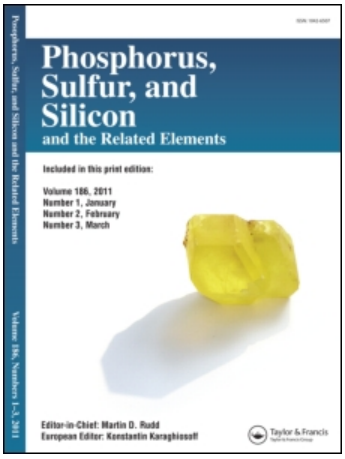

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New Synthesis of Selenophenes and Condensed Ring Systems from Ketene Dithioacetals

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New Synthesis of Selenophenes and Condensed Ring Systems from Ketene Dithioacetals

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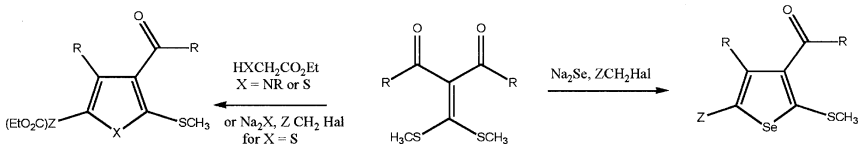
New selenophenes were prepared from ketene dithioacetals. Isoselenocyanates were used to acceded to aminoselenophenes. Starting from substituted methylsulfanylselenophenes thieno- and selenolo-selenophenes were synthetized.

Keywords Aminoselenophenes; ketene dithioacetals; selenolo[2,3-b]selenophenes; selenophenes; thieno[2,3-b]selenophenes

We have shown recently that ketene S,S dithioacetals are very useful intermediates for the construction of thiophenes[1] and pyrroles[2] (Scheme 1).



SCHEME 1 Preparation of five-membered heterocycles.

As the reaction seeems to proceed via an addition-elimination pathway before cyclization, we extended the method to the synthesis of selenophenes by using sodium selenide and activated halides (Scheme 1).

The ketene S,S dithioacetals were prepared from various active methylene compounds what allows the formation of differently functionalised selenophenes[3] (Table I).

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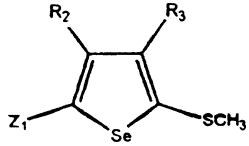
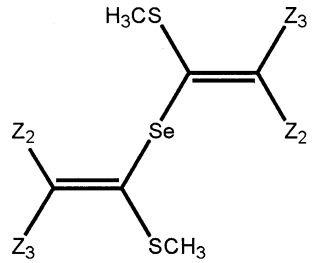
TABLE I Selenophenes Synthetized



Z_1	R_2	R_3	Yield
CO_2Et	Me	Ac	26
Ac	Me	Ac	32
CN	Me	Ac	55
PhCO	Me	Ac	40
Ac	NH_2	CN	9
CN	NH_2	CN	4
PhCO	NH_2	CN	10
PhCO	OH	CO_2Et	52
CN	OH	CO_2Et	62
CN	Me	PhCO	14

In some cases the yields in selenophenes were low. In fact in these examples, formation of the heterocycle was limited by a side reaction forming diselenides (Scheme 2).



$Z_2 = Z_3 = CN$: 86%

$Z_2 = Z_3 = Ac$: 58%

$Z_2 = CN\ Z_3 = CO_2Et$: 92%

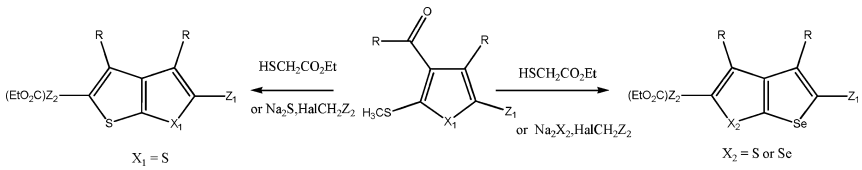
SCHEME 2 By-products in the synthesis of selenophenes.

In the case of methylsulfanyl-thiophenes we could show that the methylsulfanyl group could be used as a leaving group and allowed the formation of thieno[2,3-b]thiophenes[1] (Scheme 3).

We have used the same strategy with the methylsulfanyl-selenophenes prepared and reacted them with thioglycolates or a combination of sodium sulfide and activated halides[2] (Scheme 3).

Differently functionalized thieno[2.3-b]thiophenes could be prepared by this way (Table II).

Unfortunatly starting from 3-amino 4-cyano selenophene and 3-carbethoxy 4-methyl selenophene did not allow the formation of the



SCHEME 3 Synthesis of condensed bicyclic derivatives.

corresponding diamino or hydroxy compound. It has to be remarked that methylsulfanyl-thiophenes did not undergo the Nucleophilic Aromatic Substitution with sodium selenide to afford the same derivatives.

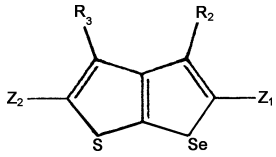
The synthesis of seleno[2,3-b]selenophenes was made in the same way by reacting methylsulfanyl-selenophenes with sodium selenide and activated halides[4] (Scheme 3).

Depending on the starting material, different functions could be introduced onto the bicyclic system (Table III).

Thieno[2,3-b]thiophenes can be made by using active methylene compounds, carbon disulfide, base and halides.[5] Taking the method over to seleno[2,3-b]selenophenes would imply the use of the very smelly carbon diselenide. Our method permit to avoid the use of it.

We have also shown that aminothiophenes can be prepared from phenyl isothiocyanates.[6] We have transposed the method to the preparation of aminoselenophenes. We have chosen to use the stable benzoyliminoisoselenocyanate described by Heimgartner et al.[7] The condensation of the isoselenocyanate in basic media with malononitrile

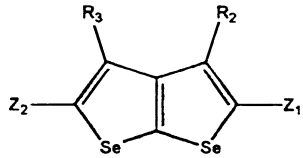
TABLE II Thieno[2,3-b]selenophenes Prepared



Z_1	R_2	R_3	Z_2	Yield
CO_2Et	Me	Me	CO_2Et	97[a]
CN	Me	Me	CO_2Et	78[a]
CN	Me	Me	PhCO	72[b]
PhCO	Me	Me	CO2Et	92[a]
PhCO	Me	Me	CN	93[b]
Ac	Me	Me	CO_2Et	90[a]
CN	Me	Ph	CO_2Et	86[a]

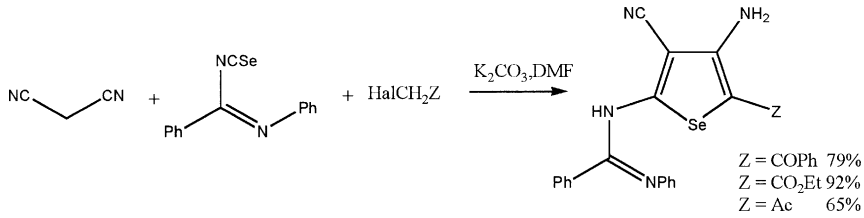
[a]With ethylthioglycolate.
[b]With Na_2S and appropriate halide.

TABLE III Selenolo[2,3-b]selenophenes Prepared



Z1	R2	R3	Z2	Yield
PhCO	Me	Me	CO_2Et	33
PhCO	Me	Me	Ac	33
PhCO	Me	Me	PhCO	42
CN	Me	Me	CO_2Et	56
CN	Me	Me	PhCO	38
Ac	Me	Me	CN	46

(as active methylene compound) and halides allowed the preparation of new amino-selenophenes (Scheme 4).



SCHEME 4 Synthesis of aminoselenophenes.

To summarize, using the reactivity of ketene S,S dithioacetals, we have developed new methods for synthetizing selenophenes. The latter could be used for the preparation of thieno- and seleno[2,3-b]selenophenes. From isoselenocyanate, we could prepare new aminoselenophenes. The selenophenes and condensed derivatives prepared having different functions allow us to envisage many transformations.

Ketene S, S and N, S acetals have been used in our Laboratory to synthetize thiophenes, pyrroles and condensed ring systems.[1–4] We have extended the method for the preparation of selenophenes[5] and selenolo-and-thieno condensed bicyclic compounds (Scheme 1). The ability of introducing various functionnal groups by this methology opens numerous synthetic possibilities.

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