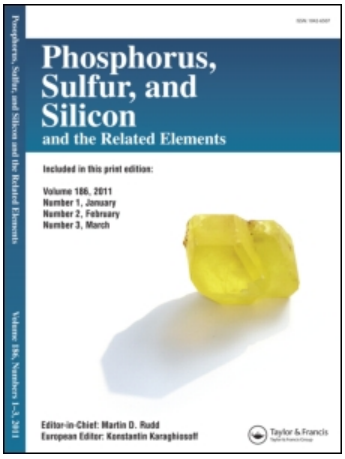

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Mlostoń, Grzegorz(1999) 'New Adventures with Thioketones and Related Compounds', Phosphorus, Sulfur, and Silicon and the Related Elements, 153: 1, 217 — 234
To link to this Article: DOI: 10.1080/10426509908546436
URL: http://dx.doi.org/10.1080/10426509908546436

Phosphorus, Sulfur and Silicon, 1999, Vol. 153-154, pp. 217-234
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New Adventures with Thioketones and Related Compounds

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Introduction

In a series of recent papers we were able to add further arguments to the opinion that thioketones are not only useful starting materials for syntheses of sulfur-containing organic compounds but can also be used as interesting models for studying mechanisms of organic reactions [1]. Due to a special ability of the thiocarbonyl group to enter cycloaddition reactions, thioketones were found to be extremely useful reagents in 1,3-dipolar cycloadditions and hetero-Diels-Alder syntheses. Another interesting point concerns the application of thioketones and other thiocarbonyl compounds to the generation of sulfur-centered 1,3-dipolar species such as thiocarbonyl ylides, thiocarbonyl S-imides, thiocarbonyl S-sulfides (thiosulfines) and thiocarbonyl S-oxides (sulfines). A new topic in the studies which is directed towards the chemistry of thioketones, concerns their transformations induced by „naked" fluoride anions.

Conversions of Thioketones Induced by the Fluoride Anion

The fluoride anion F^- is known as a very basic but poor nucleophilic species which has found many important applications in organic synthesis [2]. Silylation procedures with derivatives of trimethylsilane includes the fluoride anion as an efficient and unique catalyst. Despite the fact that many inorganic fluorides have been used as a source of fluoride anions, the use of tetrabutylammonium fluoride $(C_4H_9)_4N^+F^-$ (TBAF), which is soluble in some organic solvents (e.g. THF), led to the best results. However, in some instance the use of an aprotic solvent like toluene or pentane offers some advantages [3]. In the early 90's, Olah and Prakash [4] reported a new, simple trifluoromethylation procedure for ketones which employed (trifluoro-

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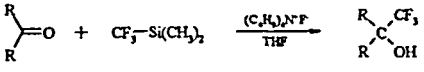
methyl)trimethysilane, $CF_3Si(CH_3)_3$, generally known as „Ruppert's reagent" (CF_3-TMS) (*Scheme 1*) [4].

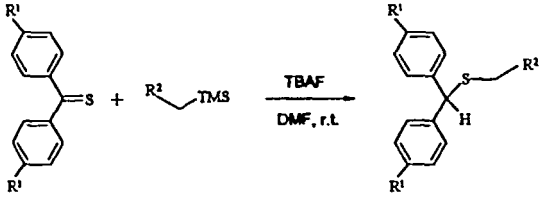


[4]

yields 60-90%

Scheme 1

The question emerged as to how thioketones would behave under analogous conditions. Reports on reactions between thiocarbonyl compounds and silylating agents are very scarce and are practically limited to two papers by Degl'Innocenti *et elab.* who reported the regioselective formation of benzyl- and allyl-thioethers after reactions of thiobenzophenone and its 4,4'-disubstituted derivatives with benzyltrimethysilane, $C_6H_5CH_2$-$Si(CH_3)_3$, or allyltrimethysilane CH_2=CH-CH_2-$Si(CH_3)_3$, respectively (*Scheme 2*) [6,7]. The products from the *„thiophilic"* addition of nucleophilic alkyl moieties were the only one detected. In their second paper they rationalized the course of the reactions as being induced by an interaction between the thioketone and silane. This reaction may well be extended to other different thiocarbonyl compounds, such as dithioethers and cyclic or linear thiocarbonates [7].



[6,7]

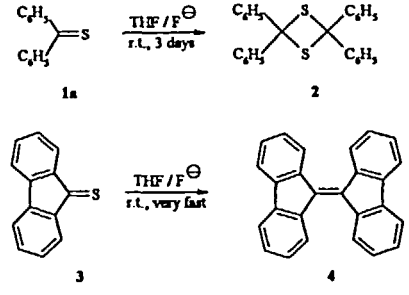
R^1 = H, Me or OMe

R^2 = Ph, or CH_2=CH-

Scheme 2

Our first concern was to determine if the fluoride anion interacts with the C=S double bond and if a possible activation achieved in this way could modify the chemical properties of thioketones.[1]

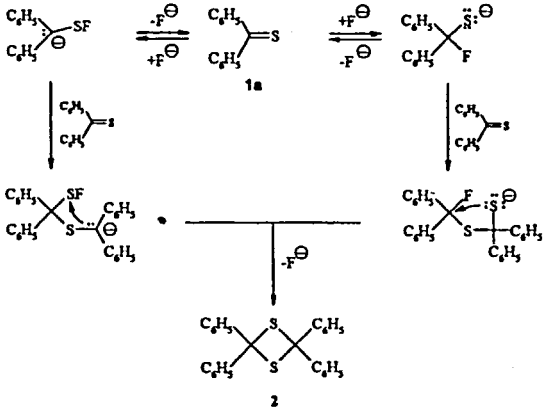
A blue solution of thiobenzophenone (**1a**) in anhydrous THF containing catalytic amounts of dry TBAF turned colorless after three days and subsequent chromatographic separation resulted in the isolation of a colorless, crystalline material which was identified as 2,2,4,4-tetraphenyl-1,3-dithiete (**2**), a formal tail-head dimer of **1a**. Despite the fact that some aliphatic thioketones were found to give analogous derivatives of 1,3-dithiete under basic conditions [9], it turned out that dimers of aromatic thioketones of this type have never been obtained in pure form. The chemical shift of the ring sp^3-carbon atoms was found at 59.7 ppm ($CDCl_3$) and was high-field shifted when compared with the carbon atoms found in the 5-membered 2,2,5,5-tetraphenyl-1,2,4-trithiolane at 92.6 ppm ($CDCl_3$), respectively [10].



Scheme 3

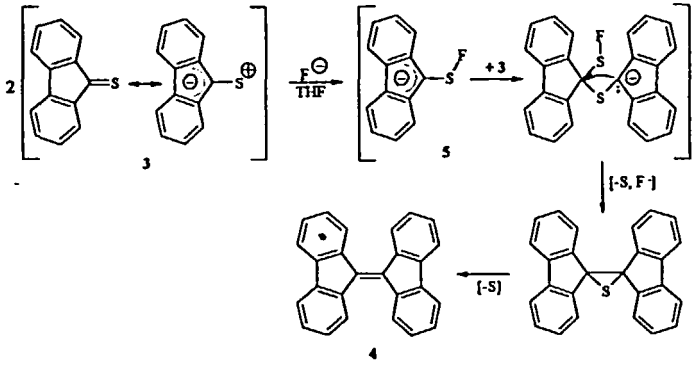
The next candidate to be examined under identical conditions was thiofluorenone (**3**) which is widely used as a model representative of very reactive (*superdipolarophilic*) aromatic thioketones [11]. In our experiments, the first drops of a dry TBAF solution added to **3** dissolved in anhydrous THF, induced a very fast conversion which changed the initial green-olive color of the solution of **3** to red-orange. After ^1H NMR analysis and simple work-up it turned out that in this case the only product formed from **3** in the presence of a catalytic amount of the fluoride anion was *bis*-fluorenylidene (**4**).

[1] Two years ago as we started this project there were no papers describing conversions of thiocarbonyl compounds mediated by fluoride anions. Only recently a series of reports originating from a German laboratory provided the initial information about the very rich chemistry involving the reactions of carbon disulfide CS_2 initiated by fluoride anions has been published [8].



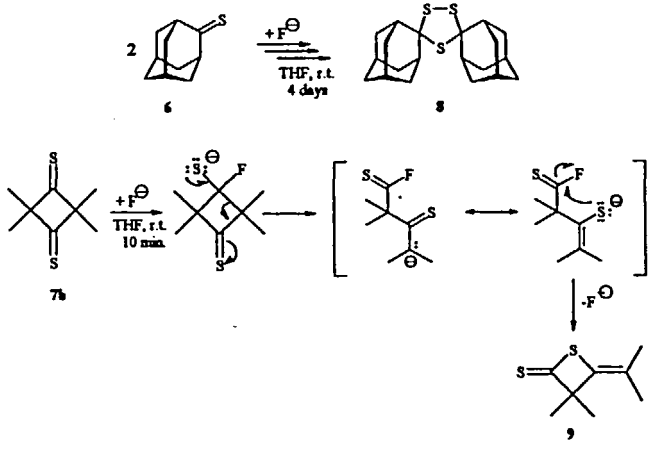
Scheme 4

A plausible rationalization of both observations is based on the assumption that the fluoride anion is able to activate thioketones and to initiate intermolecular reactions in which the regiochemistry depends clearly on the structure of the thioketone used. In the case of **1a** both types of activation, named as *thiophilic* or *carbophilic*, respectively, can be taken into account to explain the initiale step of this smooth dimerisation (*Scheme* 4). The electron density distributions along the C=S double bond in **1a** and **3** differs significantly and in the latter case it is represented by a structure with separation of the π-electron pair, as presented in *Scheme 5*. According to this scheme we postulate an initial addition of the fluoride anion to the sulfur atom (*thiophilic activation*) and formation of the thiirane, which subsequently undergoes a spontaneous desulfurization to give **4**, which is a well known substance [12].



Scheme 5

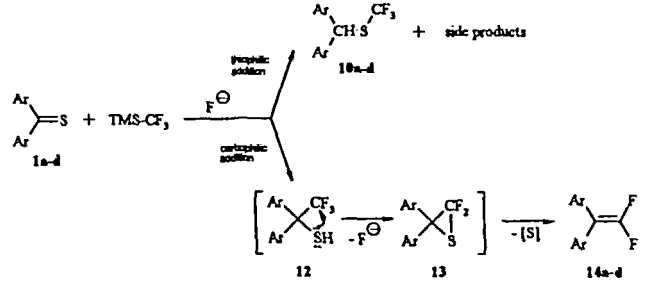
Adamantanthione (6), sterically crowded 2,2,4,4-tetramethyl-3-thioxocyclobutanone (7a) and its dithione analogue 7b are relatively stable and non-odorous cycloaliphatic thioketones which are favorite representatives of this class of compounds [11,13].



Scheme 6

In the presence of fluoride anions, **6** converted unexpectedly into di-*spiro*-1,2,4-trithiolane **8**, which is known from our recent studies and its identification was possible *via* simple comparison of the ^{1}H- and ^{13}C-NMR spectra [14]. The reaction was rather slow at room temperature and decolorisation of the orange THF solution took fourth days at ambient temperature. At the moment there is no a clear explanation of the mechanistic pathway of this clean conversion but a thiirane as an intermediate is plausible sulfur donor participating in the formation of adamantanethione *S*-sulfide involved in the formation of the final product.

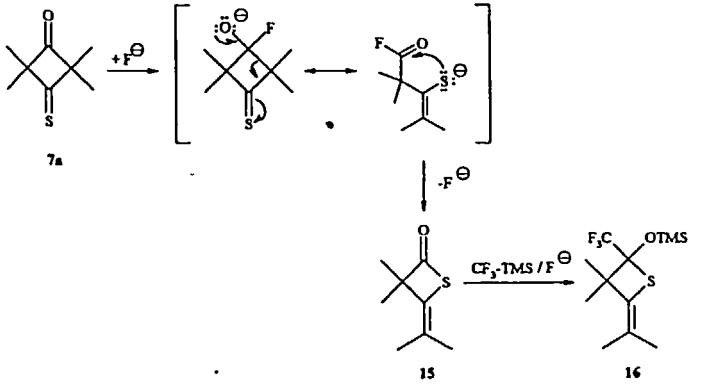
The reaction with dithione **7b** was much faster and resulted in isomerisation of the cyclobutane derivative to the dithiolactone **9**. In this case, the mechanism of isomerisation can be rationalized step by step starting from the assumption that the basic fluoride anion initiates the ring opening, as presented in *Scheme 6*. It is noteworthy that the same product was obtained by other authors using sodium methanoate as a typical strong base able to open the ring of **7b** [15].



Scheme 7

Reactions of **1a** and its 4,4'-disubstituted analogues **1b-d** with Ruppert's reagent were carried out in anhydrous THF solution in the presence of TEBA as a catalyst.[2]. Crude reactions mixtures were examined by ^{19}F-NMR and the spectra showed the presence of two fluorinated products formed in rather low yields (5-20%). The chromatographically isolated oily main products were identified as benzhydryl(trifluoromethyl)thioethers **10a-d**, which were accompanied by smaller amounts of *gem*-difluoroethylenes **14a-d** (*Scheme 7*). Other compounds isolated and fully characterized in the case of **1a** only, were non-fluorinated side products - tetraphenylthiirane and tetraphenyl-ethylene. Formation of the thioethers **10** results

from the *thiophilic* attack of the CF_3-TMS on the C=S bond and *gem*-difluoroethylenes **14** are secondary products resulting from *carbophilic* addition followed by an intramolecular substitution, as presented in *Scheme 7*.



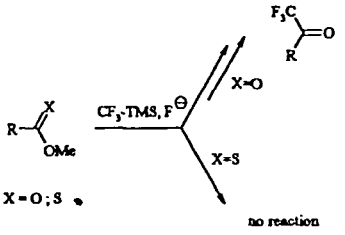
Scheme 8

An unexpected course of reaction was observed with 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**7a**) and CF_3-TMS. After a very fast conversion, an oily product **16** with molecular formula $C_{12}H_{21}F_3SiOS$, which corresponds to an 1:1-adduct, was formed quantitatively and its isolation was easily achieved by vacuum distillation. The mechanistic pathway is presented in *Scheme 8* and the first step must involve isomerisation of the starting material, induced by nucleophilic addition of the fluoride anion to the carbonyl group, leading finally to the thiolactone **15**. This step is followed by a slower addition of the Ruppert's reagent to the carbonyl group.

In a recent paper we described that unlike the previously reported observation [4], non-activated carboxylic esters very easily undergo trifluoromethylation with CF_3-TMS[2] in the presence of the „naked" fluoride anion [3]. In contrast to the case for ketones, and probably due to the lower rate of CF_3-TMS addition to the ester carbonyl group, rigorously anhydrous conditions had to be employed for these reactions in order to avoid hydrolytic decomposition of the Ruppert's reagent in the presence of TBAF to give CHF_3 (gas evolution) and TMS-OH.

[2] Without the catalyst Ruppert's reagent did not react with thioketones even after some days at ambient temperature.

Toluene or pentane were used as solvents and all reagents were thoroughly dried with freshly



Scheme 9

activated molecular sieves. To compare the reactivity of the carboxylic esters and their thio-analogues we attempted to react CF_3-TMS with methyl thio- and dithiobenzoate. In both experiments CF_3-TMS was shown again to be less reactive towards the thiocarbonyl group than towards its parent oxygen analogues. In conclusion: unlike earlier reported effective benzylations and allylations of dithioesters and even their S-oxides by using silylating reagents [6], our attempts to carry out similar trifluoromethylation using CF_3-TMS were in vain.

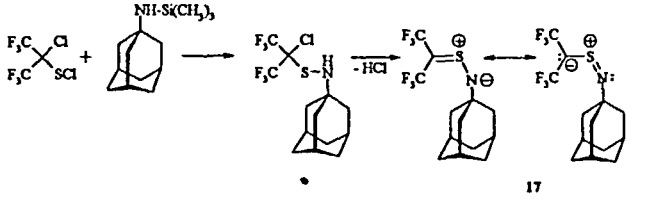
New Reactions of a Hexafluorothioacetone *S*-Imide

Thione *S*-imides, which are structurally similar to thiocarbonyl *S*-ylides and *S*-sulfides (thiosulfines), belong to the less known group of so called „sulfur-centered" 1,3-dipoles [16,17]. Fabian calculated the distribution of the electron density in the parent thioformaldehyde *S*-imide and found that it actually corresponds more closely to the structure of a 1,3-dipole than to a heterocumulene used sometimes to describe this and other similar molecules [17]. Thione *S*-imides are mostly postulated as unstable intermediates to rationalize reaction pathways and only a few cases of isolable representatives have been described hitherto. In the early 90's, Roesky *et elab.* published an efficient protocol for synthesis of a stable hexafluorothioacetone *S*-imide 17 substituted at the nitrogen atom with 1-adamantanyl skeleton [18].

Reactions of thioketones with thiocarbonyl *S*-methylides and *S*-sulfides (thiosulfines) have

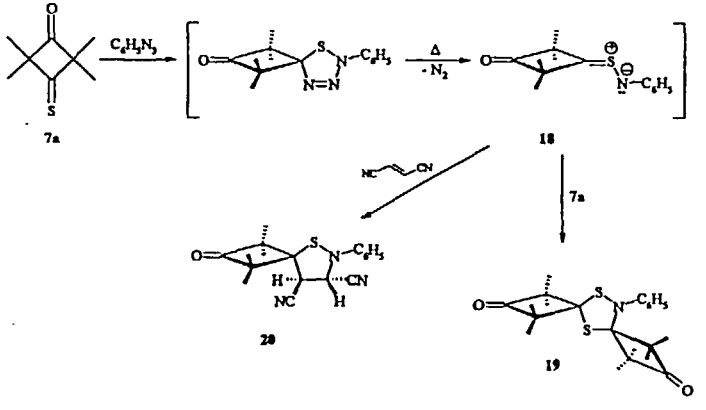
recently been studied extensively and in many cases they can be used for syntheses of 1,3-dithiolane or 1,2,4-trithiolane derivatives, respectively [1,19,20]. Reports concerning similar

conversions with thiocarbonyl *S*-imides, however are very rare and there is only one paper in



Scheme 10

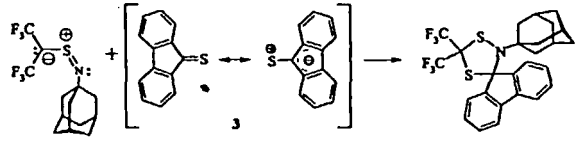
which the formation of fairly unstable [3+2]-cycloadducts of aromatic thioketones with a thione *S*-imide has been described [21].



Scheme 11

In one of our recent papers, using a completely different methodology, we rationalized unexpected formation of 1,4,2-dithiazolidines **19** in reactions of aryl azides with **7a** as resulting from the interception of the intermediate thione *S*-imide **18** by an equivalent of the unconverted starting C=S-dipolarophile [22]. Another time, the same intermediate was successfully trapped in a stereospecific manner using fumarodinitrile. The *trans*-configuration of the 1,2-thiazolidine derivative **20** was confirmed by means of a single crystal X-ray diffraction analysis [23].

We also found that N-(1-adamantanyl)-hexafluorothioacetone *S*-imide (17) reacted very quickly with aromatic thioketones at room temperature, e.g. [3+2]-cycloaddition with thiofluorenone (3) was completed after 1 min. at ambient temperature [24]. The structure of the isolated, crystalline 1,4,2-dithiazolidine 21 was also elucidated by X-ray crystallography (Fig. 1).



17 21

Scheme 12

It is known that 6 reacts with 1,3-dipoles rather more slowly than aromatic thioketones do [11] and this prediction has been confirmed in the reaction with hexafluorothioacetone *S*-imide 17. At ambient temperature, no reaction was observed and conversion was complete only after heating the reaction mixture in a sealed tube at 100 °C for ca. 2 h.

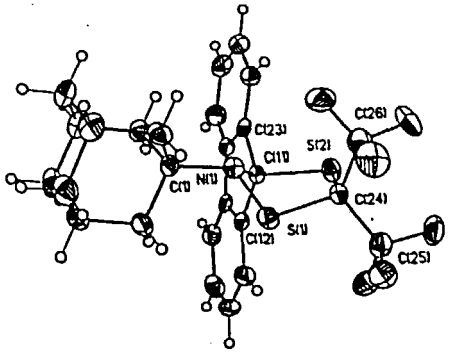
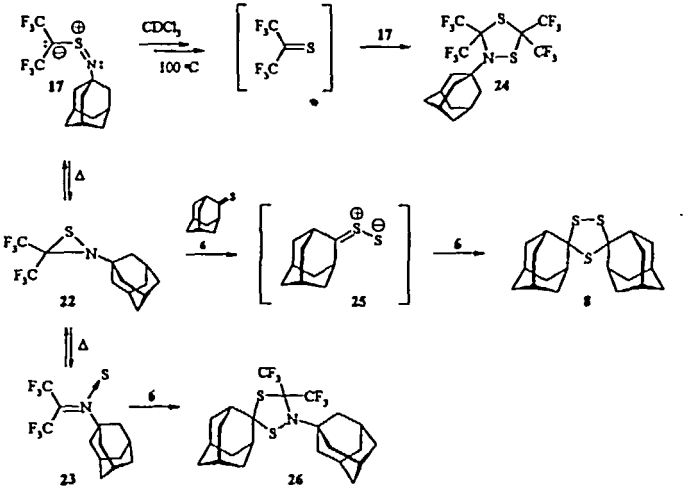


Figure 1. Crystal structure of 21 with anisotropic displacement parameters depicting 50 % probability. Only one of the two molecules which are present in the asymmetric unit is shown for clarity. Selected bond distances (Å) and angles (°) [all the values averaged over the two crystallographically independent molecules]: N(1)-C(11) 1.470(6), C(11)-S(2) 1.864(5), S(2)-C(24) 1.1.805(6), C(24)-S(1) 1.804(6), S(1)-N(1) 1.733(4), N(1)-C(1) 1.517(6), N(1)-C(11)-S(2) 104.3(3), C(11)-S(2)-C(24) 97.7(3), S(2)-C(24)-S(1) 107.7(3), C(24)-S(1)-N(1) 93.9(2), S(1)-N(1)-C(11) 109.2(3), C(12)-C(11)-C(23) 112.0(4), C(25)-C(24)-C(26) 111.0(5).

Chromatographic separation afforded three compounds which were identified as 1,4,2-dithiazolidines **24**, and **26**, and 1,2,4-trithiolane **8**, respectively. Unexpectedly, the structure of **26** didn't correspond with the structure of the *S*-imide incorporated in the heterocyclic ring and a rearrangement had to take place prior to the final cycloaddition step.



Scheme 13

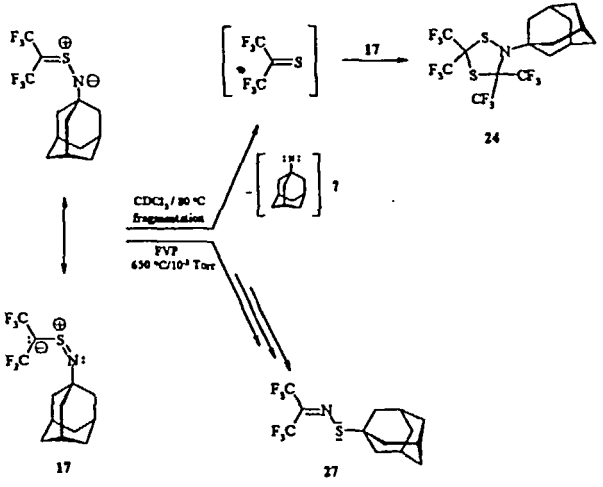
Actually, the course of the reaction leading to **26** probably involves thionitrone **23**, generated thermally from **17** in a cascade of reactions shown in *Scheme 13*.

In an extension of our studies on the 1,3-dipolar reactivity of **17**, the reaction with *trans*-cyclooctene was carried out and after a fast, exothermic conversion, the crystalline cycloadduct was isolated in almost quantitative yield [28].

In several papers published recently, we postulated thiaziridines as key intermediates in the transfer of sulfur [S] to the C=S bond, which resulted in the *in situ* generated thiosulfines [25]. The goal of a series of another experiments has been directed towards the elaboration of a protocol which would possibly offer a simple access to an isolable thiaziridine.

Thione *S*-imide **17** was selected as an ideal candidate for further experiments which attempted to achieve cyclization to a stable thiaziridine **28** substituted with two stabilizing CF_3-groups at

C-3 and a bulky 1-adamantanyl moiety at the nitrogen atom. Thermolyses and photolyses of several thione *S*-imides described in the literature always afforded the imine compounds as products of the desulfuration of the postulated intermediate thiaziridines [26]. However, no example of an isolable or at least detectable thiaziridine has yet been described [27].

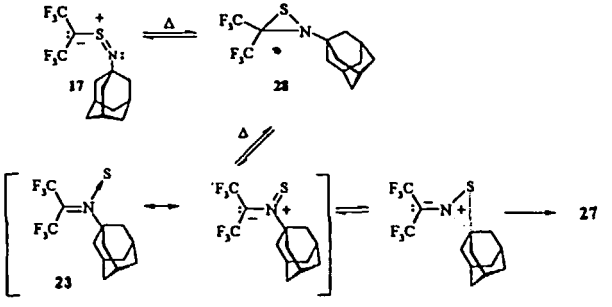


Scheme 14

Heating of 17 in $CDCl_3$ solution afforded 1,4,2-dithiazolidine 24 (known from our earlier studies with 6 and 17 [24]) as the only product isolated after fractional crystallization. Preliminary examination of the crude reaction mixture by ^{13}C NMR confirmed that it was actually the major product formed in the solution.

A completely different reaction course was observed when *S*-imide 17 was subjected to flash vacuum thermolysis (FVP) at 650 °C and 10^{-3} Torr. A crystalline, colorless product with m.p. 56-57 °C obtained after clean conversion revealed after elemental analysis the molecular formula $C_{13}H_{15}F_6NS$ which is identical with the starting material. The dream about obtaining the first isolable thiaziridine collapsed when crystallographer Dr A. Linden at Zurich University determined that the molecular structure of this product was the thiooxime ether 27 [28].

A plausible rationalization of these two completely different courses of thermolyses in solution and in the gas phase is presented in *Scheme 14* and *Scheme 15*. Due to solvatation effects, heating of the *S*-imide **17** probably leads to its dissociation of the molecule into hexafluorothioacetone and 1-adamantanylnitrene which is supposed to undergo subsequently hitherto unknown reactions resulting in formation of unstable products.



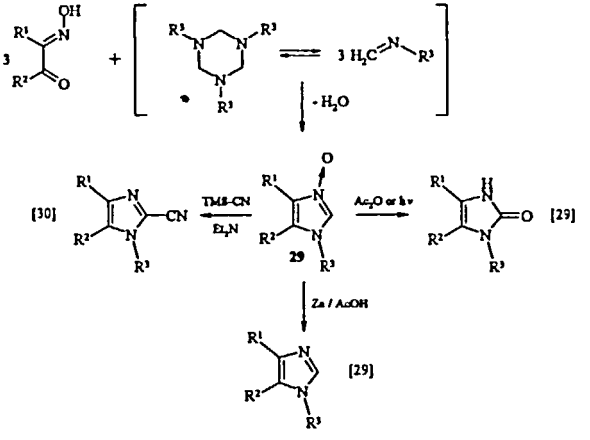
Scheme 15

Hexafluorothioacetone is supposed to be a superior dipolarophile and reacts very quickly with equimolar amounts of **17** to give **24**. On the other hand, reaction in the gas phase is an example of a cascade process which involves the electrocyclic ring closure of **17** leading to the expected thiaziridine **28** (*Scheme 15*). The final result suggests that this reactive heterocycle isomerises and exists in an equilibrium with thionitrone **23** which is postulated as an actual precursor of the thiooxime ether **27**. Strong polarisation of the electron density in the thionitrone **23** makes this unusual rearrangement, involving three-center cationic intermediate **28**, possible.

Novel Examples of the Sulfur-Transfer in Reactions of Some Azaheterocyclic N-Oxides with Thioketones

Some twenty years ago we elaborated a procedure for the preparation of 2-unsubstituted imidazole N-oxides **29** by heating 1,3,5-hexahydrotrizines with α-diketone monoximes in boiling ethanol and studied some of their reactions, which included photochemical and acetic anhydride mediated isomerisation to 2-imidazolones, desoxygenation procedures and, recently, cyanation under very mild conditions using trimethylsilylcyanate TMS-CN [29,30].

The central unit of azaaromatic N-oxides resemble nitrones which are known as active 1,3-dipoles. Some N-oxides of type **29** were successfully combined with such dipolarophiles as dimethyl acetylenedicarboxylate (DMAD) and phenyl isocyanate according to general rules of [3+2]-dipolar cycloaddition [31,32].



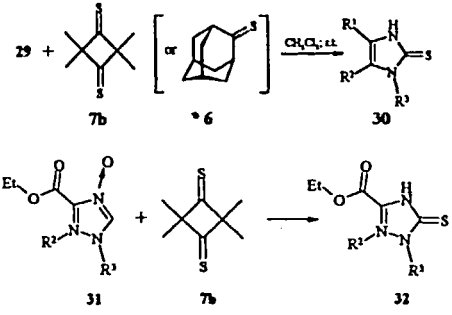
Scheme 16

However, the primary non-aromatic cycloadducts usually underwent a cascade of reactions which resulted in rearomatization of the system, e. g. the primary cycloadduct obtained from 1-benzyl-4,5-diphenylimidazole 3-oxide and phenyl isocyanate eliminated carbon dioxide and spontaneously converted into N-phenyl 1-benzyl-4,5-diphenylimidazole-2*(3H)*-amine [32].

To the best of our knowledge there has been no example of a reaction between an azaaromatic N-oxide and a thioketone reported until the present. Due to our current interest in cycloaddition chemistry involving thiocarbonyl compounds, we decided to examine whether imidazole N-oxides of type **29** are able to undergo a reaction with thioketones.

To our surprise, solutions of N-oxides **29** in $CHCl_3$ or CH_2Cl_2 treated with an equimolar amount of monothione **7a** at ambient temperature underwent an exothermic reaction and within a few minutes the characteristic red color of the thioketone completely disappeared [28,29]. The products were formed in almost quantitative yields and precipitated from the reaction solutions after cooling to room temperature. They were identified by means of spectroscopic methods as imidazole-2*(3H)*-thiones **30**. The same reaction was observed using

dithione **7b** or adamantanthione (**6**), however aromatic thiones reacted much more sluggishly (thiobenzo-phenone) or completely failed (thiofluorenone and *9H*-xanthene-9-thione) to convert imidazole N-oxides into the corresponding thiones.



7b **6** **30**

31 **7b** **32**

Scheme 17

Another representative of azole N-oxide, namely 1,2,4-(*1H*)-triazole 4-oxide (**31**) gave the respective thione **32** after typical treatment with **7b** [33].

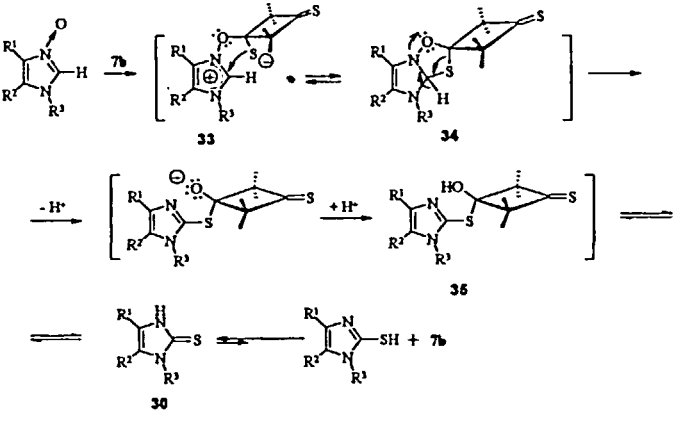
In order to study the scope and limitations of this new access to azole thiones, we used some 6-membered N-oxides, such as pyridine and pyrimidine N-oxides, but neither compound changed the red-colored solutions containing cycloaliphatic dithione **7b**. Based on this observation we concluded that the new *„S-transfer reaction"* leading to the heterocyclic thiones from N-oxides can be used efficiently only in the series of azole N-oxides.

The mechanistic pathway for the transfer of sulfur from the thiocarbonyl group to an azole ring is presented in *Scheme 18* and the first step of the reaction is a *„carbophilic"* attack of the N-oxide dipole onto the C=S group to give the zwitterionic intermediate **33** which is formally an azolium ion.

Ring closure between the S-atom and C(2) of the heterocyclic ring leads to the formal [3+2]-cycloadduct **34**. Intermediates of this type have never been observed in controlling NMR experiments, but decomposed irreversibly *via* the elusive *S*-hemiacetale **35** to yield the final products **30**.

The stepwise mechanism may also explain the failure of pyridine and pyrimidine N-oxides to react with thioketones. The key step of the conversion is the formation of the zwitterion, which in the case of 6-membered aromatic N-oxides is much less favored due to the lack of

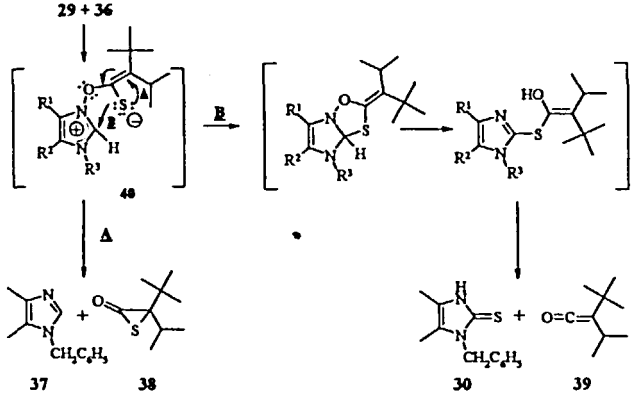
stabilization of the positive charge by the lone electron pair of the N-atom. Our interpretation involving a cascade of reactions, rather than a simple one-step 1,3-dipolar cycloaddition of the N-oxide dipole with the thiocarbonyl group, got additional support when we replaced the cycloaliphatic thioketone by *tert*-butyl-*iso*-propylthioketene (**36**).



Scheme 18

When 1-benzyl-2,3-dimethylimidazole-N-oxide was treated with an equimolar amount of **36** at ambient temperature, a slow reaction was observed which resulted in the complete decolorisation of the violet reaction solution after 2h. ^{1}H NMR examination of the crude reaction mixture confirmed the presence of desoxygenated imidazole **37** and imidazole-2(*3H*)-thione **30** in a ratio of 85:15, respectively. Furthermore, thioketene **36** was transformed into thiiranone **38**, known from earlier studies by Schaumann *et elab.* [34], in ca. 70% yield. For this conversion, in a close analogy with the earlier presented reaction pathway with thioketones, zwitterion **40** is proposed as the key intermediate (*Scheme 19*).

However, in this case the cyclisation can follow two different routes, leading to different final products. The main product, the desoxygenated imidazole, is formed *via* path A involving formation of the thiiranone **38** in eqimolar amount.



Scheme 19

The competitive pathway **B** follows reactions analogous to those discussed with thioketones as sulfur-donating reagents and results in the formation of imidazole-2*(3H)*-thione **30** along with stable *tert*-butyl-*iso*-propylketene **39**.

Acknowledgement: *Author thanks Prof. Prof. G. Olah, S. Prakash (University of Southern California), H. Huisgen (University of Munich), H. Heimgartner (University of Zurich) and H.-W. Roesky (University of Göttingen) for helpful discussions and fruitful scientific collaboration. Technical assistance of Ph.D. student T. Gendek (University of Łódź) in preparation of the manuscript is gratefully acknowledged. The Polish State Committee for Scientific Research supported research projects within „KBN-Grants" No. No. 2P303 059 05 and 3 T09A 157 10.*

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