Tetrahedron Vol. 38, No. 24, pp. 3537 to 3553, 1982
Printed in Great Britain.

0040-4020/82/243537-17$08.50/0
Pergamon Press Ltd.

TETRAHEDRON REPORT NUMBER 139

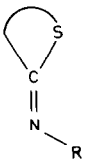
SOME RING-TRANSFORMATION REACTIONS OF SULFUR-CONTAINING HETEROCYCLES

GERRIT L'ABBÉ†
Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3030 Heverlee, Belgium

(*Received* 23 *April* 1982)

CONTENTS

Ring transformations of heterocycles constitute an important aspect of research in heterocyclic chemistry. Major contributions have been made by van der Plas (Wageningen) who has studied ring transformations under the influence of nucleophiles, and by Huisgen (München), Carrié (Rennes) and others who have carried out ring transformations by cycloaddition reactions.[1] In our research, 3-, 4- and 5-membered heterocycles **1**, having an exocyclic imine function adjacent to the S atom (cyclic thioimidates), have been considered in this respect.

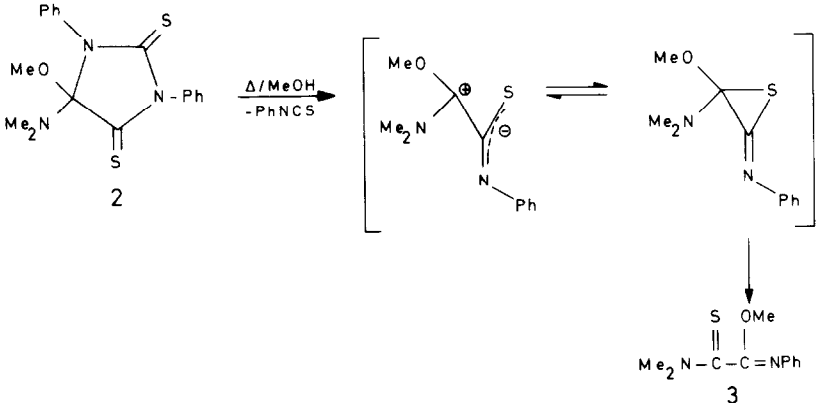


1

In this review, I shall describe the synthesis and chemistry of some representative examples studied in our laboratories, with particular emphasis on their pattern of reactivity in ring-transformation reactions.

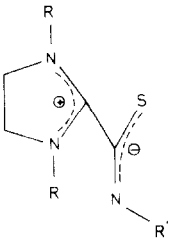
1. THREE-MEMBERED RINGS: THIIRANIMINES

Prior to our work in this field, thiiranimines had been postulated only as reactive intermediates, e.g. in the thermal conversion of the dithiohydantoin **2** into the imidate **3**.[2] Their open-chain dipolar analogues **4** and **5**, on the other hand, were well known and have been subjected to many cycloaddition reactions.[3]

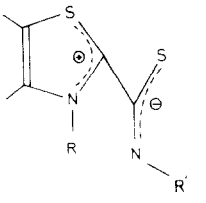


2 **3**

†Lecture given at the Annual chemical congress of the Royal Society of Chemistry, University of Aston in Birmingham, April 1982, and at the Xth International Symposium on Organic Sulphur Chemistry, Bangor, September 1982.



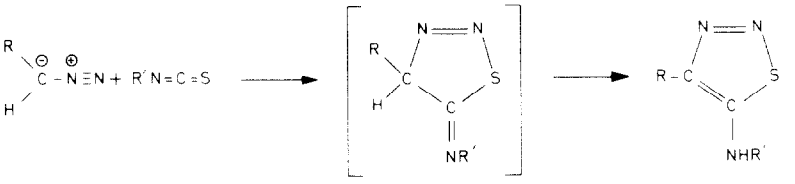
4



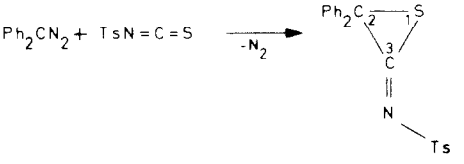
5

In principle, thiiranimines should be accessible via the reactions of diazoalkanes with isothiocyanates after loss of nitrogen. All publications on this subject, however, dealt with diazomethane or monosubstituted diazoalkanes which led to the aromatic 1,2,3-thiadiazoles **6**.[4] We have found that diphenyldiazomethane combines readily with tosyl isothiocyanate at 0° with evolution of nitrogen and formation of the N-tosyl substituted thiiranimine **7** in 67% yield.[5] *p*-Chlorophenylsulfonyl isothiocyanate reacts similarly to give the corresponding thiiranimine in 70% yield.[6]

Our thiiranimine **7** exists in the ring-closed form in the solid state (X-ray) as well as in solution (IR, ^{13}C NMR). A crystal structure analysis revealed the presence of an unusually long C_2–S bond of 1.94 Å, compared with the normal C–S length of 1.84 Å of a model compound. In addition, the other two bonds C_2–C_3 (1.47 Å) and S–C_3 (1.70 Å) are shorter than would be expected from the sum of the covalent radii.

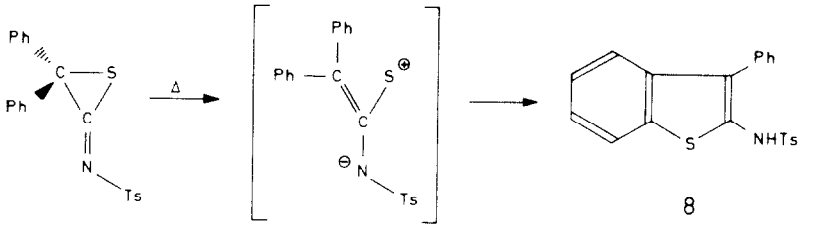


6



7

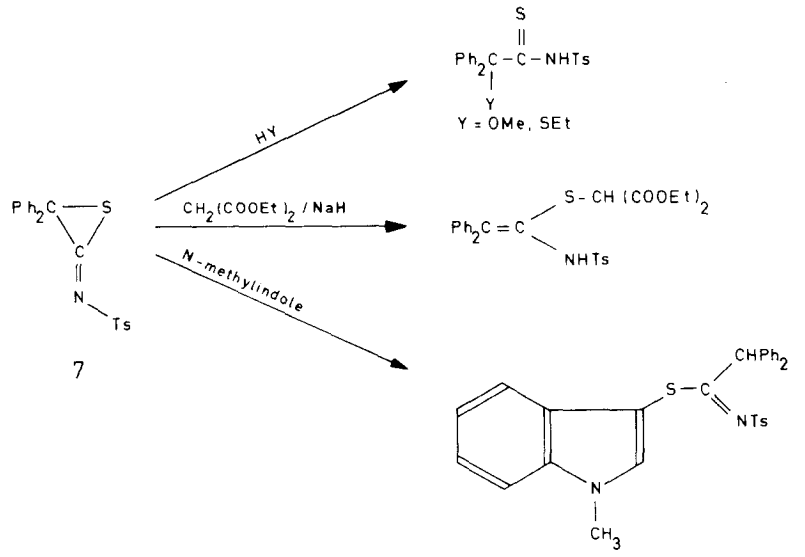
The weakness of the C_2–S bond of **7** is also reflected in its thermal lability. Upon gentle heating in a chloroform solution, it is converted quantitatively into the benzothiophene **8**. This isomerization can be interpreted in terms of a disrotatory ring-opening of **7**, followed by an electrophilic intramolecular aromatic substitution. An alternative mechanism involves an electrocyclization/aromatization process.



7 8

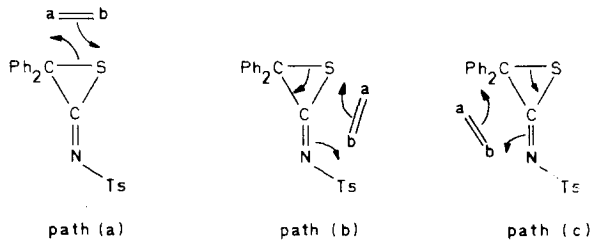
The long C_2–S bond of **7** is also cleaved by nucleophilic reagents, giving products resulting from attack at either the C_2 or S-atom, depending on the nature of the nucleophile. This ambident character of

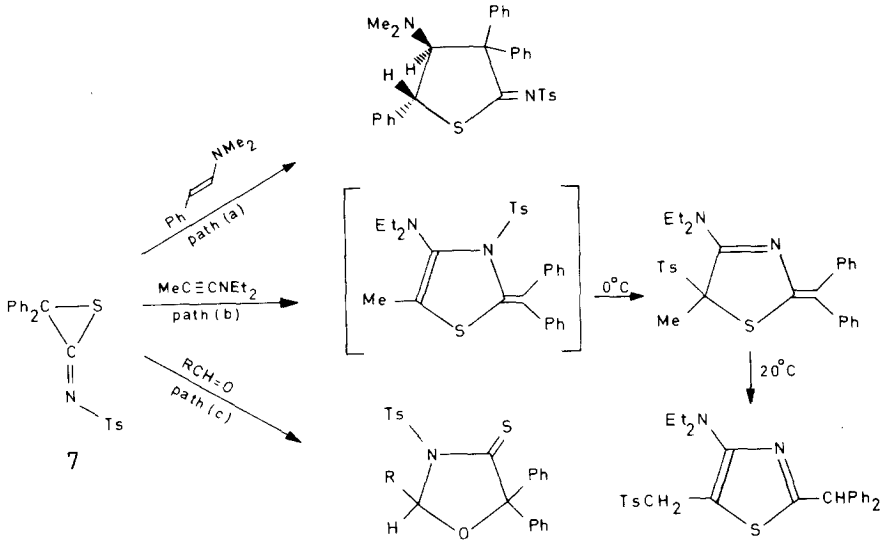
the thiiranimine is illustrated in Scheme 1.



Scheme 1.

In cycloadditions, 7 exhibits the unusual feature of reacting by any of the three possible pathways shown below:[6,7]





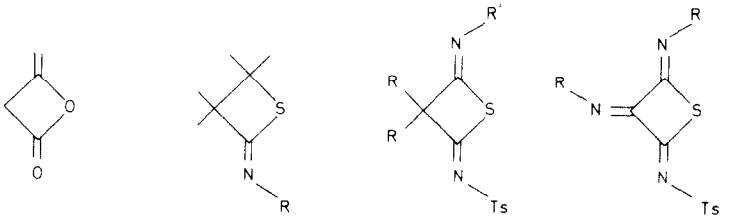
Scheme 2.

The reactions occur again by cleavage of the weak C_2–S bond and participation of either C_2 and S, N and S or C_2 and N, depending on the nature of the coreagent as exemplified in Scheme 2. The reagents behave as nucleophilic species, and no reactions are observed between **7** and thioketones, nitriles, dimethyl acetylenedicarboxylate, isocyanates, isothiocyanates, or ketenes. This contrasts sharply with the chemical behaviour of the inner salts **4** and **5** which react only with electrophilic partners in cycloaddition reactions.[3] The existence of a dipolar species or of a ring depends on the substituents and results in an "umpolung"[8] of reactivity.

The scope of ring transformations of **7** is further limited by the isomerization process **7**→**8**, which occurs under mild thermal conditions. Our attempts to prepare a more stable thiiranimine by using dimesityldiazomethane or dimethyldiazomethane instead of diphenyldiazomethane failed since neither was observed to react with tosylisothiocyanate. In this respect, it is interesting to mention that Schaumann[9] has recently succeeded in preparing other thiiranimine derivatives by reacting thioketene S-oxides with 2-amino-1-azirines. A study of their chemistry may extend our knowledge of this new ring system.

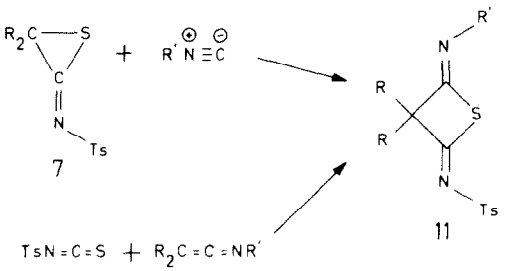
2. FOUR-MEMBERED RINGS

The well-known reactivity of diketene **9** in ring-transformation reactions is due to the presence of an extra double bond adjacent to the lactone O atom.[10] This enables the stabilization of a negative charge as an enolate anion in the open-chain intermediate, resulting from attack by nucleophilic reagents. With this in mind, we would expect a similar behaviour for bis(imino)thietanes **11** and tris(imino)thietanes **12**, but not for mono(imino)thietanes **10**.[11]



9 10 11 12

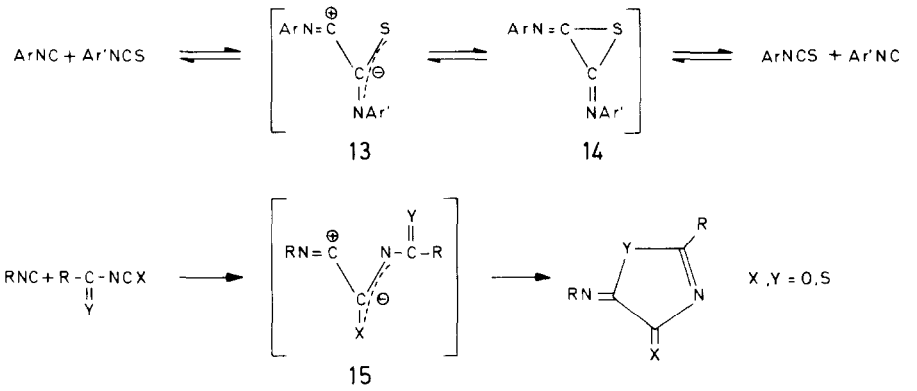
Recently, we have developed methods for the synthesis of both **11** and **12**. Thus, the bis(imino)thietanes **11** are now accessible by two methods: (i) reaction of **7** with isonitriles at 0°, and (ii) (2 + 2)-cycloadditions of ketenimines with sulfonyl isothiocyanates (Scheme 3).[12] Phenyl isothiocyanate and alkyl isothiocyanates do not react with simple ketenimines, whereas benzoyl isothiocyanate gives Diels–Alder products.



Scheme 3.

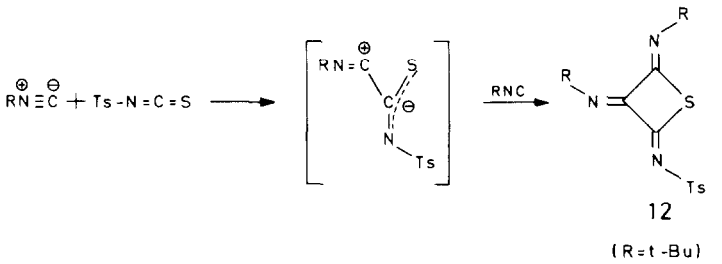
For the synthesis of the tris(imino)thietanes **12**, we were inspired by the publication of Boyer and Ramakrishnan[13] who reported the reversible transfer of sulfur from aryl isothiocyanates to aryl isonitriles (Scheme 4). This reaction is explained by the intermediacy of an externally stabilized 1,3-dipole **13** in equilibrium with the ring-closed bis(imino)thiirane **14**. Also, the reported reactions of acyl- and thioacyl substituted isocyanates[14] and isothiocyanates[15] with isonitriles occur by intramolecular

cyclization of a dipolar species **15** (Scheme 4). Attempts to trap the dipole with several potential dipolarophiles (styrene, phenyl isocyanate, acrylonitrile) had previously been unsuccessful.[14] By varying

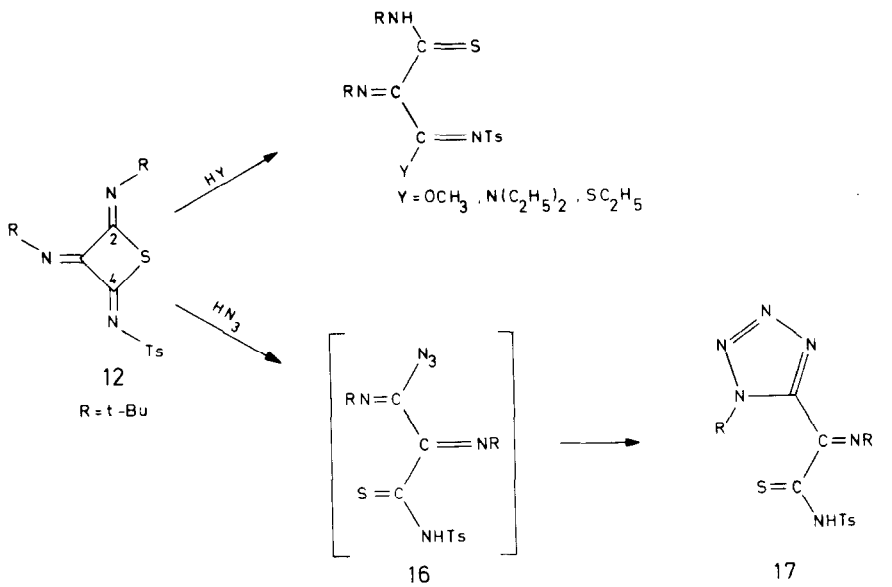


Scheme 4.

the substituents, we were able to trap the dipolar species with a second molecule of isonitrile to yield the tris(imino)thietane **12**.[16] Other sulfonyl substituted derivatives are similarly prepared in ether at 20°.

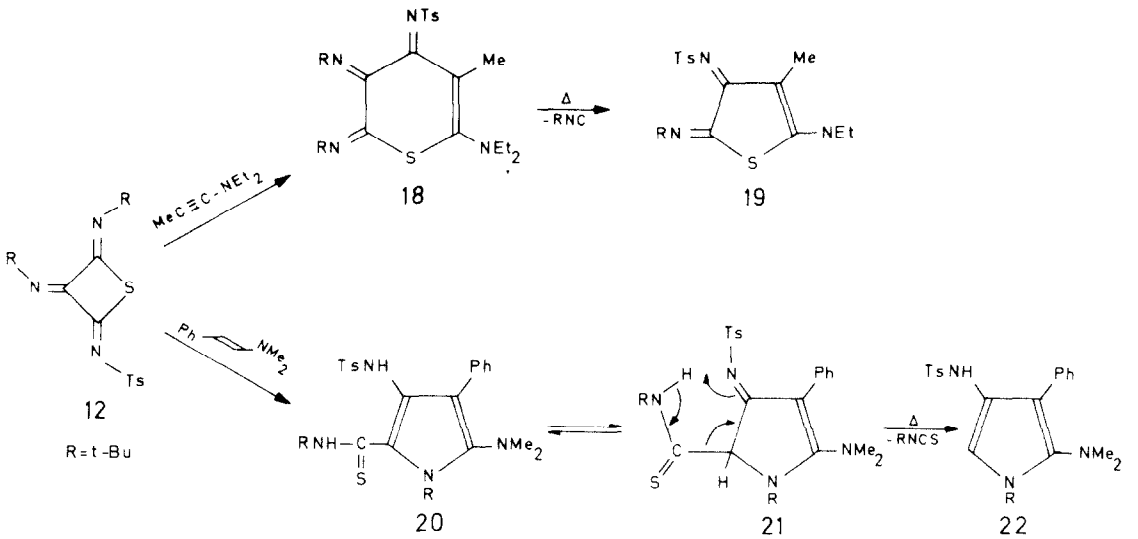


Compound **12** [as well as **11**] possesses a high reactivity at the C_4-centre towards nucleophiles (HY), resulting in C_4–S bond cleavage.[17] Some examples are shown in Scheme 5. With hydrazoic acid at 0°, a different mode of ring opening is observed, namely C_2–S bond cleavage. This is rationalized in terms of protonation of the basic imine N atom at the 2-position, followed by nucleophilic attack by the azide ion at the C_2-atom. The resulting imidoyl azide **16** then cyclizes spontaneously into the tetrazole **17** as expected.[18]



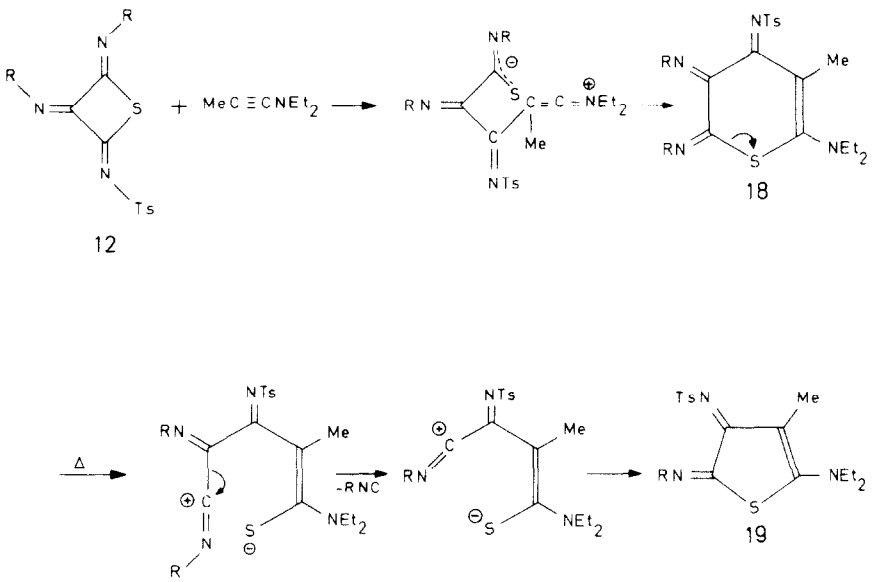
Scheme 5.

The thietane **12** with its electrophilic C_4-carbon atom is particularly reactive towards the electron-rich π-bonds of ynamines and enamines (Scheme 6).[19] The reactions occur at 0° in ether solution and furnish **18** and **20** respectively. These compounds are easily thermolyzed at 45–55° to give **19** and **22**.



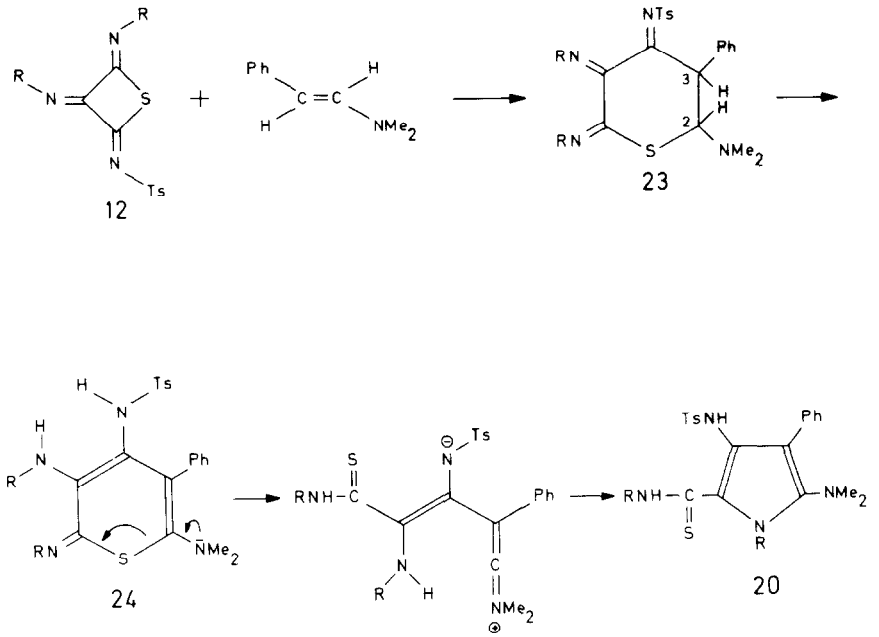
Scheme 6.

It is evident that the thiene **18** results from nucleophilic C_4–S bond cleavage of **12** by the ynamine, followed by cyclization (Scheme 6a). The further thermal conversion of **18** into the thiolene **19** is initiated by C_6–S rupture and elimination of isonitrile followed by ring closure as shown in Scheme 6a.



Scheme 6a.

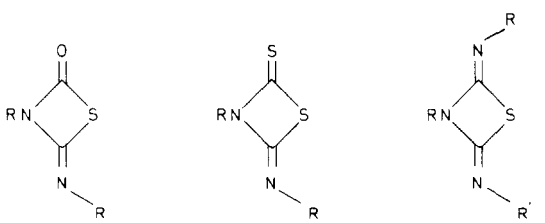
The formation of **20** from the interaction of **12** with *trans*-β-(dimethylamino)styrene may also be explained in terms of a thiane structure **23** which undergoes two tautomeric changes (first at C_3, then at C_2) to give **24** (Scheme 6b). This thopyran-2-imine is apparently unstable and undergoes ring contraction by C–S bond cleavage to give the pyrrole derivative **20**. The ^{1}H NMR spectrum ($CDCl_3$) of **20** shows the presence of the tautomeric form **21** in 10% yield. The latter is responsible for the easy elimination of t-butyl isothiocyanate and formation of **22** (Scheme 6).



Scheme 6b.

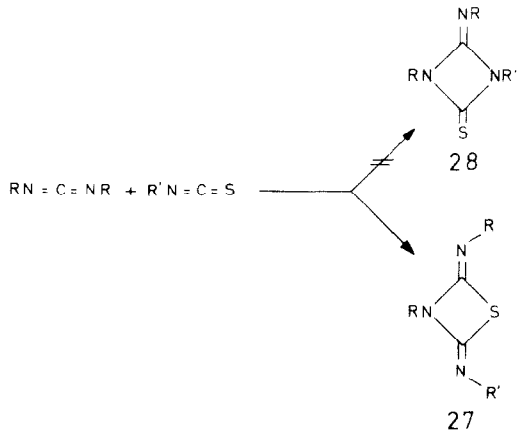
In conclusion, the three functions of **12** may be involved in ring-transformation reactions. Hence, crystal structure analysis is undoubtedly useful in elucidating the correct structure of the products.[19,20]

Another series of interesting candidates for ring-transformation reactions are the thiazetidinimines **25**, **26** and **27**. Both **25** and **26**, having aryl R-substituents, have long ago been reported in the German literature.[21,22] They are accessible by the reactions of thioureas with phosgene and thiophosgene respectively. Freund and Wolf[22] also mentioned that **26** is converted into **25** upon treatment with mercury oxide. Recently, Fahrenholtz *et al.*[23] re-invented the synthesis of **26**, apparently without knowledge of the German work.



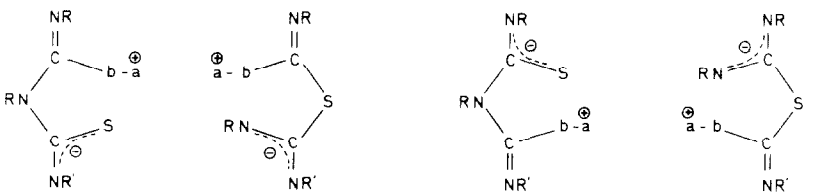
Since the early publications on the synthesis and some decomposition reactions of **25** and **26**, these have received little attention.[24] Of particular interest is the ring system **26** which may be considered as the formal dimer of an isothiocyanate, although it does not exist in equilibrium with the latter. We have studied their ring-transformation reactions.[25]

Bis(imino)thiazetidines **27** are of more recent date. They are prepared by the cycloaddition reactions of isothiocyanates preferentially activated by electron-withdrawing groups (such as Ts, COOEt, $P(S)Ph_2$, p-$NO_2C_6H_4$) with carbodiimides. The adducts were first formulated as having a 1,3-diazetidine ring structure **28**,[26] but later revised in favour of **27**.[27]

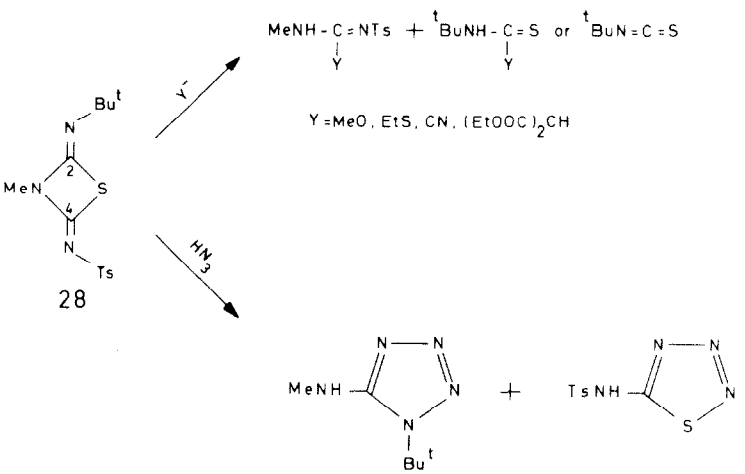


Dondoni *et al.*[28] have investigated the mechanism of this reaction and concluded that the kinetic data (high negative ΔS^*, small ΔH^*, small solvent dependence on rate) and the failure to trap open-chain intermediates tend to favour a concerted mechanism in which the carbodiimide is the suprafacial and the isothiocyanate the antarafacial component.

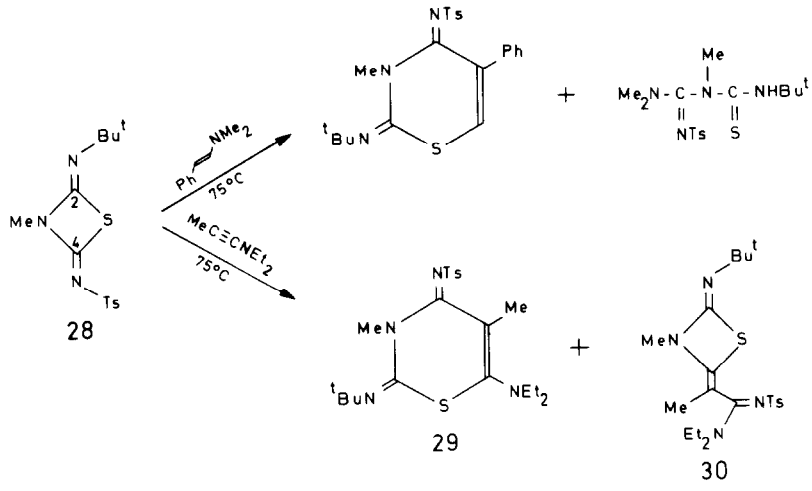
A priori, several pathways can be considered for the reactions of **27** with nucleophiles or electron rich π-systems (a = b). Attack may occur at either the C_2 or C_4 centre with formation of four types of intermediates (Scheme 7). In the case of unsaturated reaction partners, each of the intermediates has two possibilities for ring-closure leading to 6-membered heterocycles which, in addition, are potential candidates for a Dimroth-rearrangement.[29] These considerations prompted us to study the chemistry of a selected example **28**, previously prepared by Ulrich[27] from methyl-t-butylcarbodiimide and tosyl isothiocyanate. The results are shown in Schemes 8 and 9.[30]



Scheme 7.



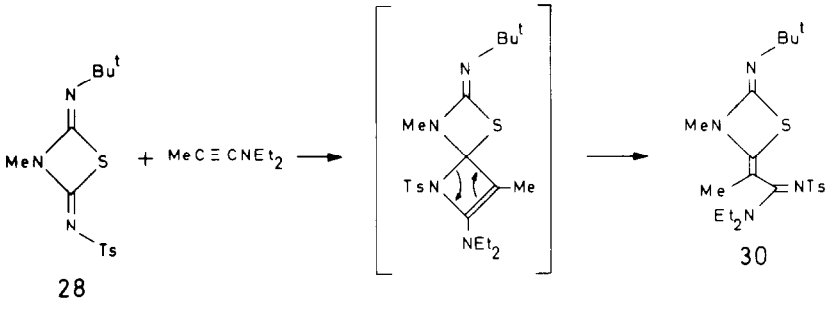
Scheme 8.



Scheme 9.

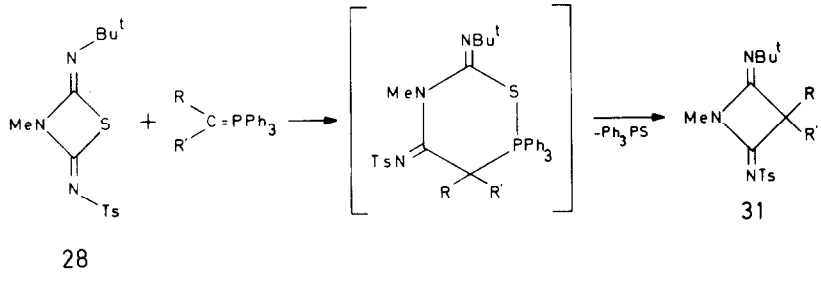
Scheme 8 illustrates the possibility of attacking the ring at two sites C_4 (with nucleophiles) and C_2 (with hydrazoic acid). In the first case, this leads to the elimination of t-butyl isothiocyanate which could then combine with a second molecule of nucleophile. In the reaction with hydrazoic acid, the C_2=N function of **28** is first protonated and then attacked by the azide ion, leading to extrusion of tosyl isothiocyanate. The ultimate products are a tetrazole and a thiatriazole. Since all the reactions are carried out at room temperature, no cycloreversion of **28** occurs prior to addition of the nucleophile.

The 6-membered rings obtained from **28** and enamines or ynamines (Scheme 9) result from C_4–S bond cleavage and re-cyclization by the S atom. N,N-diethylaminopropyne and **28** yield in addition to the expected thiazine **29** a new thiazetidine **30**. The formation of this product is explained by a (2+2)-cycloaddition of the ynamine at the C=NTs function of **28**, followed by valence isomerization (Scheme 9a).



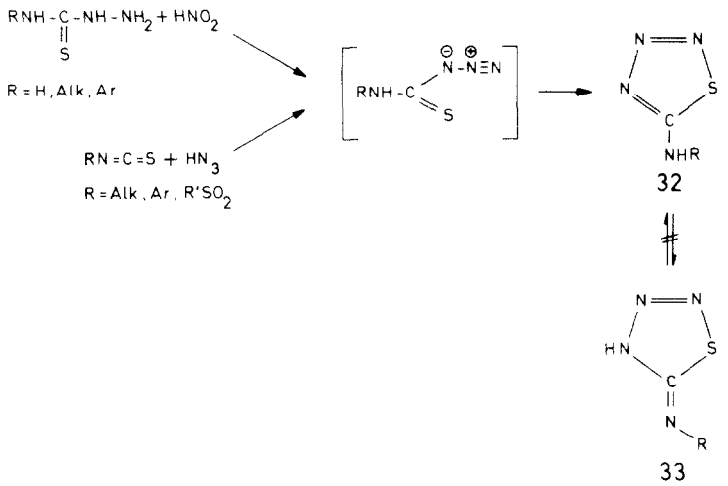
Scheme 9a.

Another interesting aspect of **28** is its reaction with disubstituted methylenetriphenylphosphoranes to give the previously unknown class of bis(imino)azetidines **31**.[31] A P-containing 6-membered ring is probably formed as intermediate which subsequently collapses to **31** by elimination of triphenylphosphane sulfide. The synthetic potential of this reaction is being studied in detail.



3. FIVE-MEMBERED RINGS

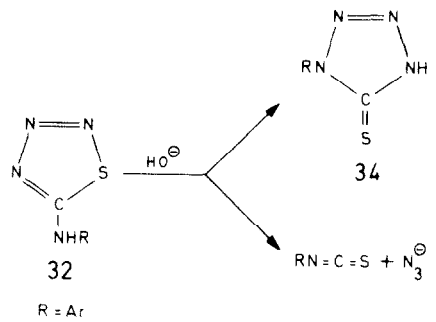
5-Amino-1,2,3,4-thiatriazole and alkyl substituted derivatives **32** were first prepared, and their structure correctly assigned by Freund in the nineteenth century.[32] They were obtained by treatment of thiosemicarbazide and 4-alkylthiosemicarbazides with nitrous acid. 4-Arylthiosemicarbazides were later shown to react analogously.[33] Another method developed for the preparation of 5-(monosubstituted)amino-1,2,3,4-thiatriazoles is the treatment of isothiocyanates with hydrazoic acid (Scheme 10).[34] This method can also be used for the synthesis of sulfonyl substituted derivatives.[35] Spectroscopic methods have established that the compounds exist only in the amino form **32** and not in the tautomeric imino form **33**.[34,36]



Scheme 10.

In spite of the long history of aminothiatriazoles, no ring-transformation reactions have been reported, except for the base-induced isomerization of 5-arylamino-1,2,3,4-thiatriazoles **32** into the corresponding tetrazolin-5-thiones **34**.[33] This transformation is promoted by the presence of electron-withdrawing aryl substituents, but even then the yields are low (up to 37%) due to competitive degradation into isothiocyanates and azide ion (Scheme 11).

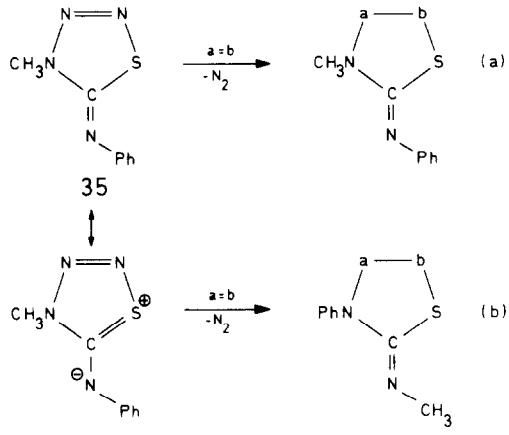
Our investigations have been focused on derivatives of the imine form **33** which were expected to undergo ring-transformation reactions with unsaturated substrates with loss of nitrogen. This research has led to the discovery of some interesting pathways which vary according to the nature of the substituent (aryl/alkyl, sulfonyl or acyl) introduced on the imine N atom.



Scheme 11.

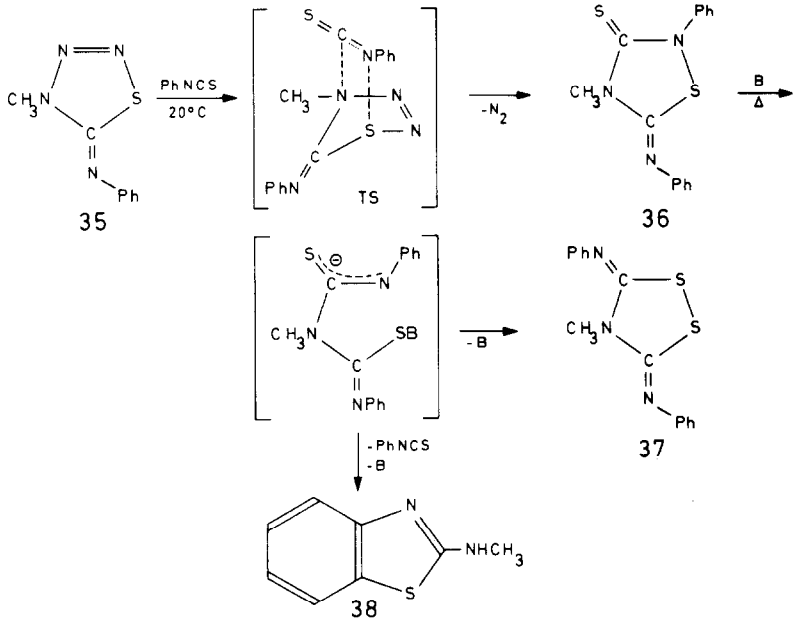
4-Methyl-5-phenylimino-1,2,3,4-thiatriazoline **35** has been reported to result from the reaction of **32** (R = Ph) with diazomethane.[37] In fact, this reaction also furnishes the exocyclic methylated product in nearly the same amount.[38] Compound **35** undergoes cycloaddition/elimination reactions with heterocumulenes at room temperature by second order kinetics according to the two pathways shown in Scheme 12. Isocyanates, alkyl isothiocyanates and aryl isothiocyanates react by path (a),[38,39] whereas the

electrophilic acyl isothiocyanates and sulfenes follow path (b) where **35** reacts as a masked 1,3-dipole.[40] Ketenes were found to react by both pathways.[40,41]



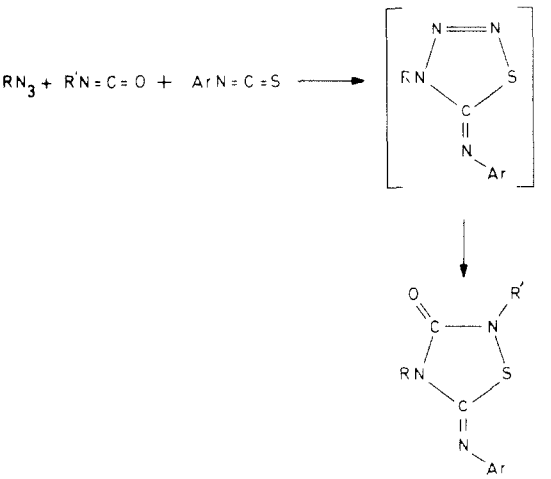
Scheme 12.

The cycloadducts obtained in Scheme 12 are candidates for further ring-transformation reactions by a Dimroth rearrangement.[29] For instance, the reaction of **35** with phenyl isothiocyanate at room temperature yields the thiadiazolidine **36** as the major product (78%) in addition to the dithiazolidine **37** (18%) and a small amount of benzothiazole **38** (4%) (Scheme 13).[38] Since **36** isomerizes into **37** with DABCO, we consider **36** as the primary product from the cycloaddition/elimination reaction [path (a) of Scheme 12]. This conclusion is supported by the results obtained from the reaction of benzyl azide with phenyl isothiocyanate at 60° where a thiatriazolinimine is postulated as an intermediate.[38] Here, the C=N adduct corresponding to structure **36** ($PhCH_2$ instead of Me) is also formed as major product in the early stage of the reaction, but it then rearranges into the C=S adduct corresponding to **37** (Ph–CH_2 instead of Me) as the reaction progresses. During this isomerization, which is promoted by azide, some decomposition into a benzothiazole occurs by elimination of isothiocyanate.



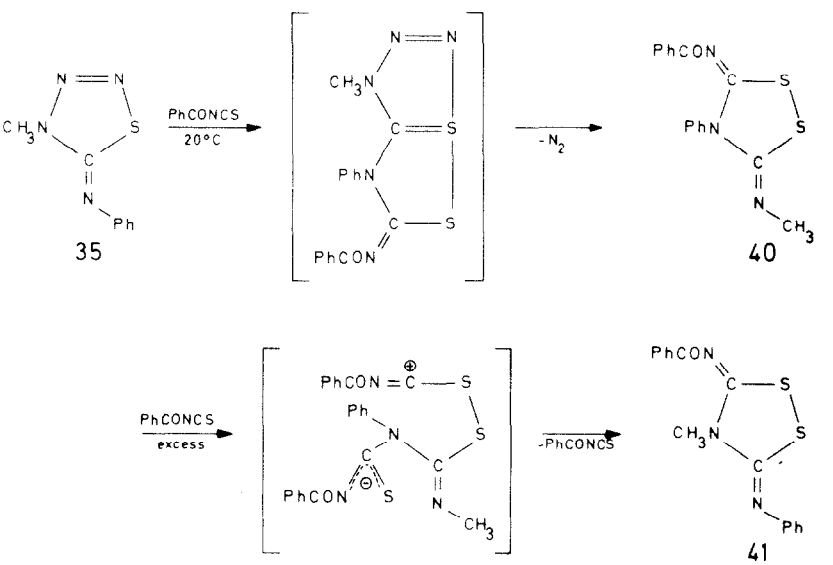
Scheme 13.

Cycloaddition/elimination reactions of **35** with isocyanates occur at the C=N bond of the heterocumulene. This has led to the discovery of a three-component reaction in which 5-arylimino-1,2,4-thiadiazolidin-3-ones **39** are prepared by combining aryl isothiocyanates with alkyl azides and isocyanates at 80°.[39] The reactions proceed via thiatriazolinimines.



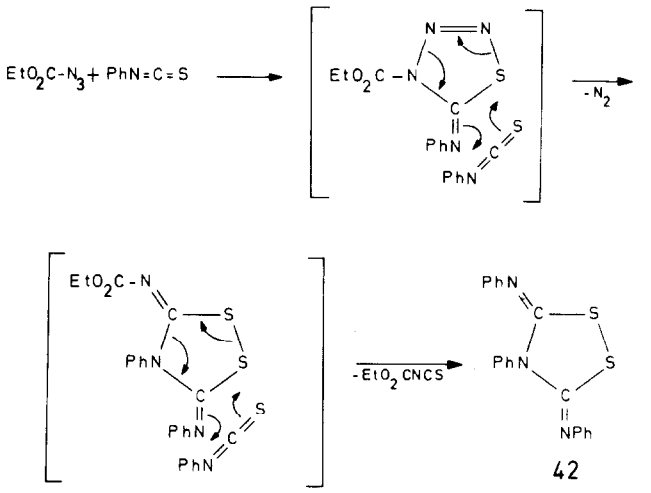
39

Dimroth rearrangements also occur in reactions which follow path (b) of Scheme 12. A typical example is the reaction of **35** with the electrophilic benzoyl isothiocyanate at room temperature where the C=S adduct **40** is formed when equimolar amounts of reagents are used.[40] In the presence of a threefold excess of benzoyl isothiocyanate, the primary product **40** rearranges by ring-opening/ring-closure into the thermodynamically more stable isomer **41** (Scheme 14). Ethoxycarbonyl isothiocyanate and sulfenes react analogously with **35**.[40] Finally, it is interesting to note that the two pathways (a) and (b) of Scheme 12 may occur by a concerted mechanism in accordance with some kinetic data, although a stepwise mechanism cannot be rigorously excluded.



Scheme 14.

On the basis of these results we can interpret the formation of the unexpected product **42** (m.p. 257°, yield 33%) from the reaction of ethyl azidoformate with phenyl isothiocyanate at 100°.[42] A plausible mechanism is outlined in Scheme 15 and involves the formation of a thiatriazolinimine, followed by two cycloaddition/elimination reactions.



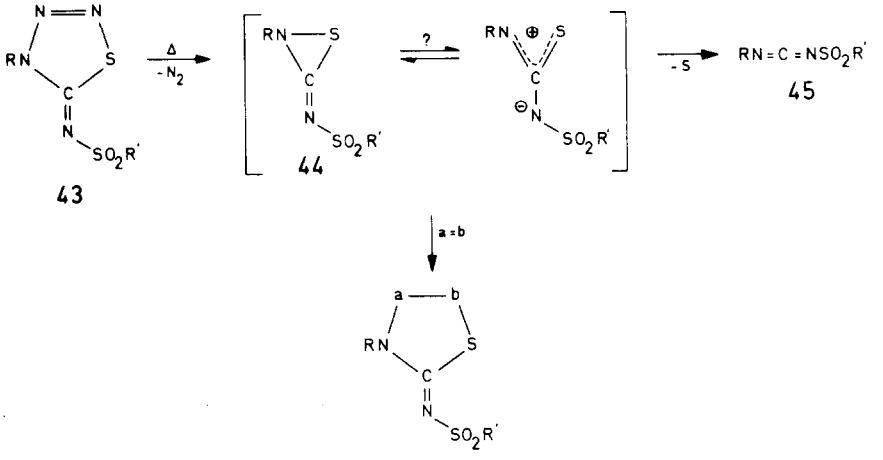
Scheme 15.

When the phenyl substituent of **35** is changed for a sulfonyl substituent, a completely different pattern of reactivity is observed. The 4-alkyl-5-sulfonylimino-1,2,3,4-thiatriazolines **43** are available by two methods: (i) cycloadditions of alkyl azides with sulfonyl isothiocyanates at room temperature[43] and (ii) methylation of sulfonylaminothiatriazoles **32** ($R = R'SO_2$) with diazomethane.[35] This latter method gives the exocyclic methylated product (in most cases as major component) in addition to **43** (R = Me).

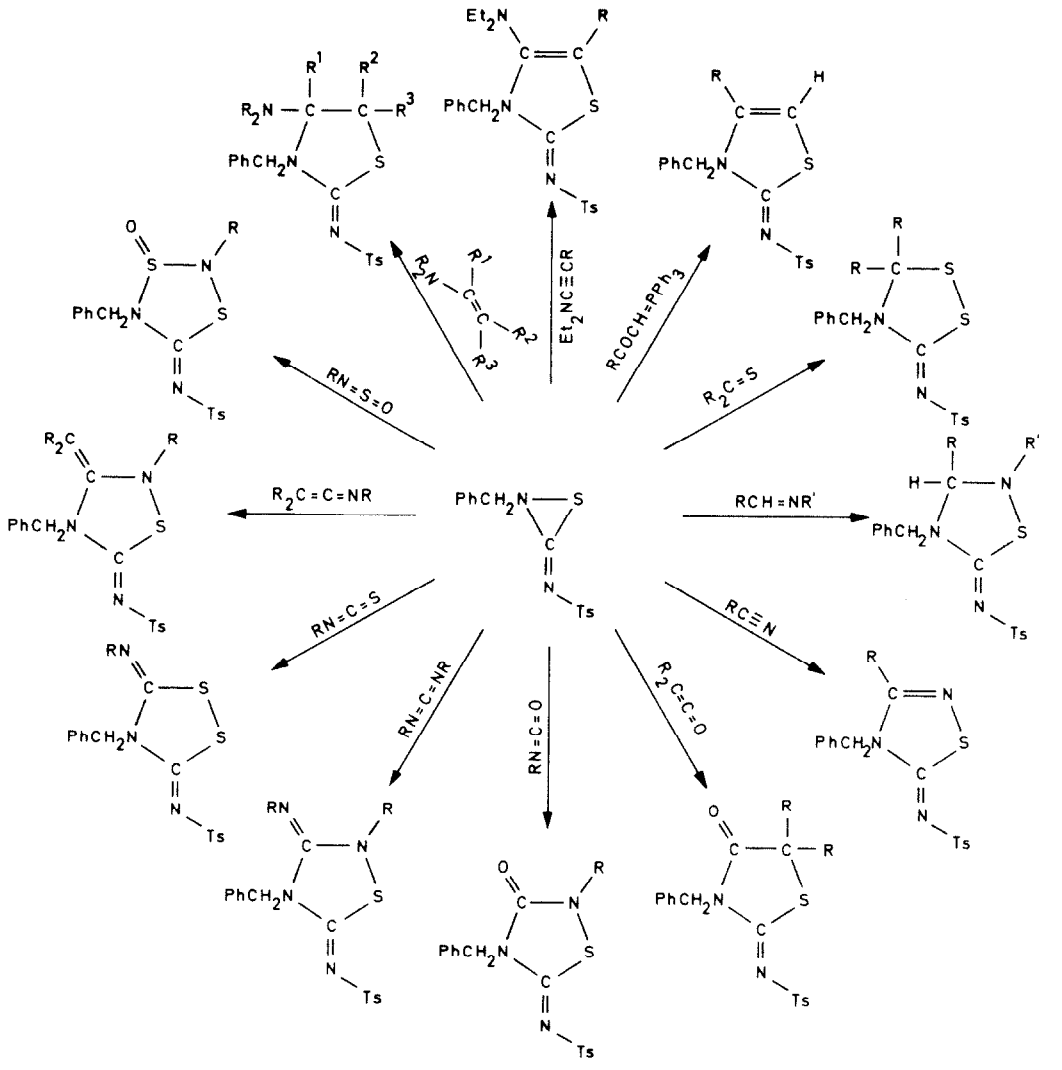
The heterocycles **43** decompose thermally at 50–80° into sulfonyl substituted carbodiimides **45** (Scheme 16).[43] A thiaziridinimine **44** and/or its ring-opened dipolar form is postulated as an intermediate since it can be trapped with unsaturated systems. The reactions are first order and independent of the nature and concentration of the trapping reagent. The synthetic potential of this pathway is illustrated in Scheme 16a for the benzyl tosyl substituted intermediate.[43,44]

In view of the different reactivities of aryl and sulfonyl substituted thiatriazolinimines, we have also considered the possibility of preparing acyl substituted derivatives **46**. A possible approach would seem to be the cycloadditions of alkyl azides with acyl isothiocyanates. However, these led to 1,2,4-dithiazolidines **47** and 1,2,4-thiadiazoles **48**.[45] The 4-alkyl-5-acylimino-1,2,3,4-thiatriazolines **46** are first formed, but they react *in situ* (50°) with a second molecule of isothiocyanate by elimination of nitrogen. Several mechanisms can be postulated for the formation of **47** and **48** from **46**, but no insight could be obtained by following the reactions by ^1H NMR since no intermediates were detected.

Another approach towards the synthesis of **46** would be the alkylation of acylaminothiatriazoles **32** (R = R'CO), but these compounds are as yet unknown. Attempts to prepare them by acylation of



Scheme 16.

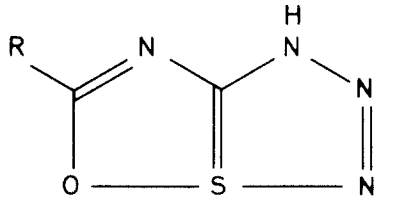


Scheme 16a.

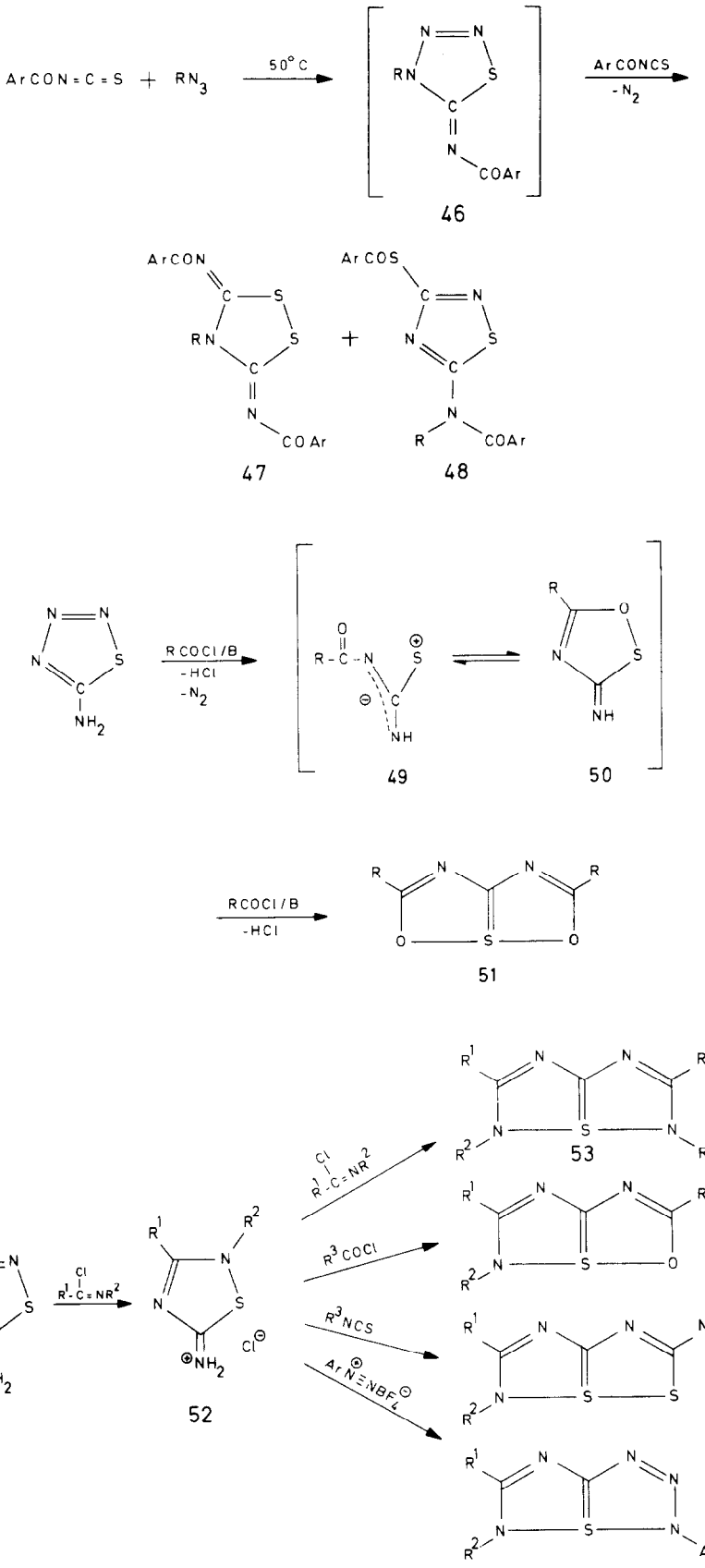
5-(unsubstituted)amino-1,2,3,4-thiatriazole **32** (R=H) in the presence of base resulted in the formation of the previously unknown class of 1,6-dioxa-6aλ^4-thia-3,4-diazapentalenes **51**.[46,47] Mechanistically, the ring-opened thiaziridinimines **49** were believed to be the key intermediates in the reaction. They undergo cyclization into **50** followed by reaction with a second molecule of acyl chloride to give **51**.†

This method can be extended to the synthesis of 1,3,4,6-tetra-aza-6aλ^4-thiapentalenes **53** (previously unknown) by using imidoyl chlorides instead of acyl chlorides. Here, the 5-imino-1,2,4-thiadiazolines **52** can be isolated as hydrochlorides from the reaction, providing the possibility of preparing symmetrical as well as unsymmetrical tetra-azathiapentalenes and other classes of thiapentalenes by using various electrophilic reagents. The results are summarized in Scheme 17.[46,48] This discovery has opened a

†Instead of **49**, a thiapentalene-like structure (i) may be considered as an intermediate. This would eliminate nitrogen to give **50**.



(i)



Scheme 17.

new field of thiapentalene synthesis of undoubtedly widespread interest.[49] Indeed, a considerable amount of research is devoted to thiapentalenes because of their unique properties of single bond/no bond resonance.[50]

Before ending, I would like to draw the attention to the stereochemistry of the molecules indicated in this review. All the crystal structure analyses which have been carried out show that the imine substituent is cis to the ring sulfur atom. This stereochemistry, however, does not necessarily reflect the situation in solution, since a fast syn-anti isomerization is in many cases expected at room temperature.[51]

Acknowledgement—I am grateful to my co-workers, whose names are quoted in the references for their enthusiastic collaboration and stimulating discussions. Financial support from the University, the F.K.F.O. and the "Ministerie voor Wetenschapsbeleid" is gratefully acknowledged. I am also indebted to Prof. W. D. Ollis (Sheffield) for valuable comments.

REFERENCES

[1]H. C. van der Plas, *Ring Transformations of* 3-, 4-, 5-, 6- *and* 7-*membered Heterocycles*, Vols. I and II. Academic Press, New York (1973); *Lect. Heterocycl. Chem.* **2**, S83 (1974); *Accounts Chem. Res.* **11**, 462 (1978); R. Huisgen, *XXIIIrd Int. Cong. Pure Appl. Chem.* **1**, 175 (1971); *Angew. Chem. Int. Ed. Engl.* **16**, 572 (1977).
[2]M. Reiffen and R. W. Hoffmann, *Chem. Ber.* **110**, 37 (1977).
[3]H. E. Winberg and D. D. Coffman, *J. Am. Chem. Soc.* **87**, 2776 (1965); A. Takamizawa, K. Hirai, and S. Matsumoto, *Tetrahedron Letters* 4027 (1968); W. Schössler and M. Regitz, *Chem. Ber.* **107**, 1931 (1974) and refs cited.
[4]B. Eistert, M. Regitz, G. Heck and H. Schwall, *Methoden der organischen Chemie* (*Houben-Weyl*) Vol. X/4, pp. 785–786, Georg Thieme Verlag, Stuttgart (1968); J. Goerdeler and G. Gnad, *Chem. Ber.* **99**, 1618 (1966); S. Hoff and A. P. Blok, *Recl. Trav. Chim. Pays-Bas* **93**, 317 (1974); M. Regitz, B. Weber, and A. Heydt, *Liebigs Ann.* 305 (1980).
[5]G. L'abbé, J-P. Dekerk, J-P. Declercq, G. Germain, and M. Van Meerssche, *Angew. Chem.* Int. Ed. Engl. **17**, 195 (1978).
[6]G. L'abbé, J-P. Dekerk, C. Martens, and S. Toppet, *J. Org. Chem.* **45**, 4366 (1980).
[7]G. L'abbé, J-P. Dekerk, S. Toppet, J-P. Declercq, G. Germain, and M. Van Meerssche, *Tetrahedron Letters* 1819 (1979).
[8]For reviews on the concept of "umpolung" see D. Seebach, *Angew. Chem.* Int. Ed. Engl. **8**, 639 (1969); D. Seebach and M. Kolb, *Chem. & Ind.* 687 (1974); D. Seebach and D. Enders, *Angew. Chem.* Int. Ed. Engl. **14**, 1 (1975).
[9]E. Schaumann, lecture at the *8th Int. Cong. of Heterocyclic Chemistry*, Graz, August (1981); *Angew. Chem.* **94**, 706 (1982).
[10]Review: T. Kato, *Accounts Chem. Res.* **7**, 265 (1974).
[11]For the synthesis of mono(imino)thietanes, see E. Schaumann, S. Sieveking, and W. Walter, *Tetrahedron* **30**, 4147 (1974); A. Dondoni, A. Battaglia, P. Giorgianni, G. Gilli, and M. Sacerdoti, *J. Chem. Soc.* Chem. Commun. 43 (1977); A. Dondoni, A. Battaglia, and P. Giorgianni, *J. Org. Chem.* **45**, 3766 (1980); A. Dondoni, A. Battaglia, F. Bernardi, and P. Giorgianni, *Ibid.* **45**, 3773 (1980); R. G. Visser, J. P. B. Baaij, A. C. Brouwer, and H. J. T. Bos, *Tetrahedron Letters* 4343 (1977); J. Mulzer and T. Kerkmann, *Angew. Chem.* **92**, 470 (1980); E. Schaumann, H-G. Bäuch, and G. Adiwidjaja, *Ibid.* **93**, 600 (1981).
[12]G. L'abbé, J-P. Dekerk, J-P. Declercq, G. Germain and M. Van Meerssche, *Tetrahedron Letters* 3213 (1979).
[13]H. J. Boyer and V. T. Ramakrishnan, *J. Org. Chem.* **37**, 1360 (1972).
[14]R. Neidlein, *Chem. Ber.* **97**, 3476 (1964); *Angew. Chem.* Int. Ed. Engl. **3**, 446 (1964); *Arch. Pharm. Weinheim* **298**, 124 (1965); J. Goerdeler and H. Schenk, *Chem. Ber.* **98**, 3831 (1965); H. Schenk, *Ibid.* **99**, 1258 (1966).
[15]J. Goerdeler and D. Wobig, *Liebigs Ann.* **731**, 120 (1970); J. Goerdeler and H. Lüdke, *Chem. Ber.* **103**, 3393 (1970).
[16]G. L'abbé, L. Huybrechts, J-P. Declercq, G. Germain and M. Van Meerssche, *J. Chem. Soc.* Chem. Commun. 160 (1979).
[17]G. L'abbé, L. Huybrechts, S. Toppet, J-P. Declercq, G. Germain and M. Van Meerssche, *Bull. Soc. Chim. Belg.* **88**, 297 (1979).
[18]Reviews: M. Tišler, *Synthesis* 123 (1973); V. Ya. Pochninok, L. F. Avramenko, P. S. Grigorenko and V. N. Skopenko, *Russian Chem. Rev.* **44**, 481 (1975); R. N. Butler, *Chem. Ind.* 371 (1973); *Adv. Heterocycl. Chem.* **21**, 433 (1977). For a theoretical study on the imidoyl azide—tetrazole isomerism, see L. A. Burke, J. Elguero, G. Leroy, and M. Sana, *J. Am. Chem. Soc.* **98**, 1685 (1976).
[19]G. L'abbé, L. Huybrechts, S. Toppet, J-P. Declercq, G. Germain and M. Van Meerssche, *Bull. Soc. Chim. Belg.* **87**, 893 (1978).
[20]For ring-transformation reactions of (11), see G. L'abbé, J-P. Dekerk and M. Mahy, *Bull. Soc. Chim. Belg.* **89**, 561 (1980).
[21]W. Will, *Ber.* **24**, 1485 (1891).
[22]M. Freund and H. Wolf, *Ibid.* **25**, 1456 (1892).
[23]K. E. Fahrenholtz, W. Benz, J. F. Blount and T. H. Williams, *J. Org. Chem.* **45**, 4219 (1980).
[24]H. Eilingsfeld, G. Neubauer, M. Seefelder and H. Weidinger, *Chem. Ber.* **97**, 1232 (1964); G. Gattow and K. Klaeser, *Z. Anorg. Allg. Chem.* **434**, 110 (1977).
[25]G. L'abbé, J-P. Dekerk and M. Deketele, *Bull. Soc. Chim. Belg.* **91**, 243 (1982); G. L'abbé, P. Vangheluwe and S. Toppet, *ibid.* in press.
[26]H. Ulrich and A. A. R. Sayigh, *Angew. Chem.* Int. Ed. Engl. **4**, 520 (1965); H. Ulrich, B. Tucker and A. A. R. Sayigh, *Tetrahedron* **22**, 1565 (1966); H. Ulrich, *Cycloaddition Reactions of Heterocumulenes*, pp. 233–235. Academic Press, New York (1967).
[27]I. Ojima and N. Inamoto, *Chem. Commun.* 1629 (1970); I. Ojima, K. Akiba, and N. Inamoto, *Bull. Chem. Soc. Japan* **46**, 2559 (1973); H. Ulrich, B. Tucker, and A. A. R. Sayigh, *J. Am. Chem. Soc.* **94**, 3484 (1972); see also O. Hritzová and P. Kristian, *Coll. Czech. Chem. Commun.* **43**, 3258 (1978).
[28]A. Dondoni and A. Battaglia, *J. Chem. Soc.* Perkin II, 1475 (1975); O. Exner, V. Jehlička and A. Dondoni, *Coll. Czech. Chem. Commun.* **41**, 562 (1976); see also G. L'abbé, L. Van Meervelt and G. S. D. King, *Bull. Soc. Chim. Belg.* **90**, 1185 (1981).
[29]Review: M. Wahren, *Z. Chem.* **9**, 241 (1969).
[30]G. L'abbé, D. Sorgeloos, S. Toppet, G. S. D. King and L. Van Meervelt, *Bull. Soc. Chim. Belg.* **90**, 63 (1981).
[31]G. L'abbé, D. Sorgeloos and S. Toppet, *Tetrahedron Letters* 2909 (1982).
[32]M. Freund and H. P. Schwarz, *Ber. Disch Chem. ges.* **29**, 2491 (1896); M. Freund and A. Schander, *Ibid.* **29**, 2500 (1896).
[33]E. Lieber, C. N. Pillai and R. D. Hites, *Can. J. Chem.* **35**, 832 (1957).
[34]Review: K. A. Jensen and C. Pedersen, *Adv. Heterocycl. Chem.* **3**, 263 (1964).
[35]R. Neidlein and K. Salzmann, *Synthesis* 52 (1975).
[36]G. L'abbé, S. Toppet, A. Willocx and G. Mathys, *J. Heterocycl. Chem.* **14**, 1417 (1977).
[37]R. Neidlein and J. Tauber, *Arch. Pharm. Weinheim* **304**, 687 (1971).
[38]G. L'abbé, G. Verhelst and S. Toppet, *J. Org. Chem.* **42**, 1159 (1977).
[39]G. L'abbé and G. Verhelst, *Angew. Chem.* Int. Ed. Eng. **15**, 489 (1976).
[40]G. L'abbé, A. Timmerman, C. Martens and S. Toppet, *J. Org. Chem.* **43**, 4951 (1978).

[41]For similar reactions of alkyl substituted thiatriazolinimines with β-dimethylaminostyrene and diphenylketene, see N. H. Toubro and A. Holm, *J. Chem. Soc.* Perkin I, 1440 (1978).
[42]G. L'abbé and M. Komatsu, unpublished results.
[43]G. L'abbé, E. Van Loock, R. Albert, S. Toppet, G. Verhelst and G. Smets, *J. Am. Chem. Soc.*, **96**, 3973 (1974).
[44]G. L'abbé, G. Verhelst, C-C. Yu, and S. Toppet, *J. Org. Chem.* **40**, 1728 (1975); G. L'abbé and C-C. Yu, *J. Heterocycl. Chem.* **13**, 883 (1976); G. L'abbé, G. Verhelst, S. Toppet, G. S. D. King and J. Briers, *J. Org. Chem.* **41**, 3403 (1976); G. L'abbé and C-C. Yu, *Chem. & Ind.* 312 (1977); G. L'abbé, A. Van Asch, J-P. Declercq, G. Germain, and M. Van Meerssche, *Bull. Soc. Chim. Belg.* **87**, 285 (1978).
[45]G. L'abbé, M. Komatsu, C. Martens, S. Toppet, J-P. Declercq, G. Germain, and M. Van Meerssche, *Bull. Soc. Chim. Belg.* **88**, 245 (1979).
[46]G. L'abbé, G. Verhelst, and G. Vermeulen, *Angew. Chem.* Int. Ed. Engl. **16**, 403 (1977); G. L'abbé and G. Vermeulen, *Bull. Soc. Chim. Belg.* **90**, 89 (1981).
[47]The acylation reactions of (32) (R = H) were independently investigated by R. J. S. Beer and I. Hart, *J. Chem. Soc.* Chem. Commun. 143 (1977). More recently, 51 has also been prepared by the bromine oxidation of 1,3-diacylthioureas, J.O. Gardner, *J. Org. Chem.* **45**, 3909 (1980).
[48]G. L'abbé, G. Vermeulen, S. Toppet, G. S. D. King, J. Aerts, and L. Sengier, *J. Heterocycl. Chem.* **18**, 1309 (1981); G. L'abbé and G. Vermeulen, *Bull. Soc. Chim. Belg.* **91**, 97 (1982).
[49]Our method has already been utilized by Y. Yamamoto and K. Akiba, *Heterocycles* **13**, 297 (1979).
[50]For a recent review, see C. Th. Pedersen, *Sulfur Reports* **1**, 1 (1980).
[51]Review: O. Sutherland, *Annual Reports on NMR Spectroscopy* (Edited by E. F. Mooney, Vol. 4, pp. 186–192. Academic Press, London (1971).