Pergamon

Tetrahedron 54 (1998) 15027–15062

TETRAHEDRON

Tetrahedron report number 475

Conversion of the Thiocarbonyl Group into the Carbonyl Group

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Received 18 September 1998

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PII: S0040-4020(98)00880-1

1. INTRODUCTION

The conversion of thiocarbonyl compounds into carbonyl compounds has attracted the interest of organic chemists since the early 19th century, first for the quantitative determination of compounds containing the thiocarbonyl moiety and later on for synthetic and mechanistic aspects. In parallel with the first methods of >C=O → >C=S conversion, a variety of methods for C=S → C=O conversion was developed. These include oxidative procedures involving inorganic and organic reagents, and hydrolytic procedures of which those catalyzed by metal ions are the most important.

To the best of our knowledge, a review dealing with >C=S → >C=O conversion does not exist in the literature, even if some aspects of the transformation are discussed in reviews of distinct thiocarbonyl compounds. It is the intent of this report to survey and update the published material on the transformation of the thione moiety by a variety of reagents leading to the replacement of the sulfur atom with the oxygen atom in acyclic and cyclic, aromatic and heteroaromatic thiocarbonyl compounds.

2. OXIDATION

The oxidation of the thiocarbonyl group in carbo-, hetero- and acyclic structures can be carried out by numerous oxidative reagents, and can lead to the disulfide cation (>C=S^+–S^+=C<), the carbonyl group (>C=O) and the methylene group (>CH_2); the latter is obtained in the field of thio-enolizable heterocyclic compounds through the oxidation of the sulfydryl moiety (>C–SH) to sulfonic acid (>C–SO_3H) which loses its sulfur atom as sulforic acid. We review all those methods which accomplish >C=S → >C=O conversion starting with the oldest.

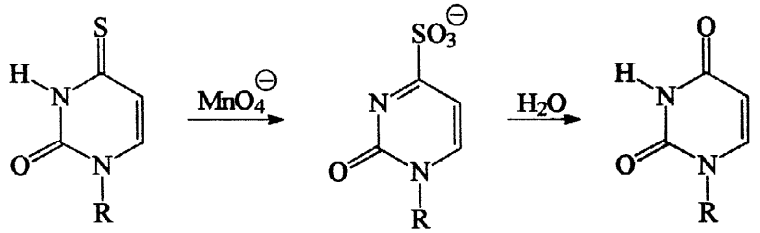
2.1. Inorganic reagents

Over the years, potassium permanganate has been the most widely used inorganic salt and it has been proved to be particularly useful in the case of heterocyclic thiones. Today, however, potassium permanganate and other salts, oxides or acids have been replaced by more selective and milder organic reagents.

2.1.1. Potassium permanganate (PP) and other inorganic salts

PP has been employed in acetonic, alkaline and neutral solutions for the conversion of thiouridines,[1] thioureas,[2-4] pyridine-2-thiones,[5] pyran-2- and 4-thiones,[6-8] thiopyran-2- and 4-thiones,[6,7,9,10] 1,2-dithiole-3-thiones,[11-16] 1,3-dithiole-2-thiones,[17] 1,2-thiazoline-5-thiones,[18] pyrazole-5-thiones,[19] 1,2,3-benzotriazine-4-thiones,[20] tetrazolo-5-thiones,[21] thiaphosphazinethiones,[22] thiohydantoins,[23] 1,3,4-triazine-2-thiones[24] and benzothiazine-2-thiones[25] into the corresponding oxygen analogues.

For thiones which cannot equilibrate with the enethiols, presumably the reaction mechanism of PP is comparable to that of olefins with the initial formation of a cyclic manganate ester.[26] A sulfonate which is stable in neutral solution, but which rapidly hydrolyzes to the carbonyl compound in acidic or basic media, is involved in the case of thiocarbonyl compounds which can tautomerize to enethiols. In the case of thiouridine,[1] for example, it was verified that after 15 minutes PP at pH 7 (phosphate buffer) gives sodium sulfonate which undergoes rapid hydrolysis to uridine upon exposure to acid or alkaline solution (Scheme 1).



R = methyl, ribofuranosyl

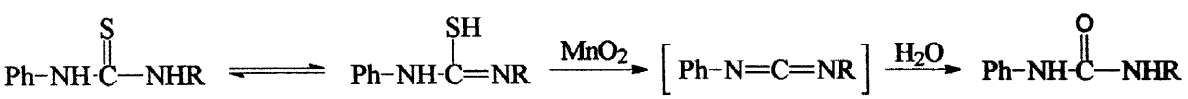
Scheme 1

An analogous conversion was accomplished by osmium tetroxide[27] and sodium metaperiodate.[28]

In the conversion of diphenylthiourea into diphenylurea,[2] PP, potassium persulfate and potassium chromate were also used in a useful comparison with sodium peroxide, while pyridin-2-thiones[5] and 1,2-dithiole-3-thiones[13,29] were treated with chromic anhydride to obtain oxygen analogues.

2.1.2. Manganese dioxide (MD)

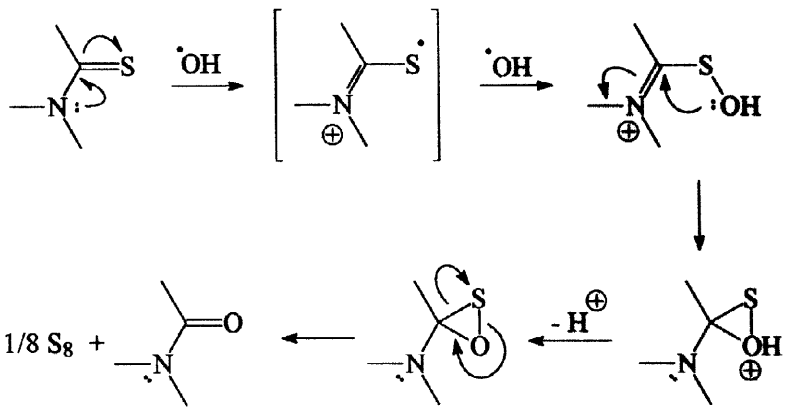
Sharma *et al.*[30] and Bhalerao *et al.*[31] oxidized thio-enolizable thioureas, thioamides and thiolactams to ureas, amides and lactams with MD by shaking the mixture of the oxidant and the substrate at room temperature. A probable mechanism suggested by Sharma *et al.*[30] for this reaction may involve the initial formation of carbodiimide (Scheme 2).



R = H, 4-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$, C_6H_5, 4-ClC_6H_4, 3-ClC_6H_4

Scheme 2

However, based on the structure of the active MD, which contains potentially labile hydroxy groups, and on the results of their experiments, Bhalerao *et al.*[31] suggested the following reaction mechanism (Scheme 3).



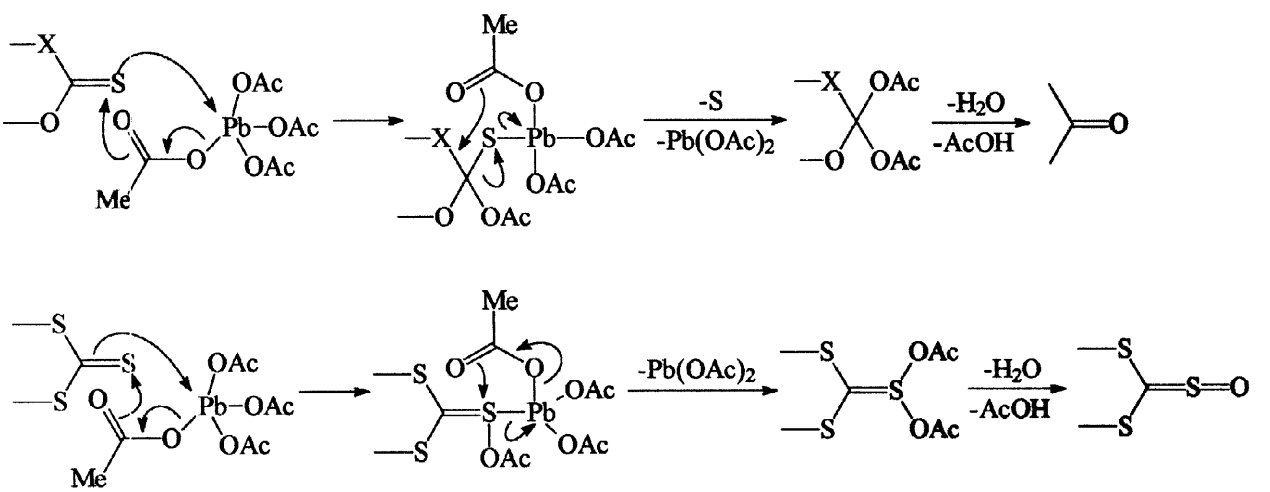
Scheme 3

2.1.3. Sodium and potassium bromate and iodate

Thioureas of types $RNHCSNH_2$ and RNHCSNHR', except phenylbenzylthiourea, were smoothly desulfurized to ureas by potassium bromate or iodate in alkaline solution, but thioureas of types $R_2NCSNHR$ and R_2NCSNR_2 were inert.[32] Wojahn and Wempe[33,34] used a bromate solution for the quantitative determination of thiourea derivatives in the oxidation and bromination steps.

2.1.4. Lead tetracetate (LT)

In their study on the reaction of LT with sugar derivatives containing a thiocarbonyl group, Doane *et al.*[35] showed that 3-O-acetyl- and 3-O-*p*-tolylsulfonyl-1,2-O-isopropylidene-α-D-glucofuranose-5,6-thionocarbonates consumed one molar equivalent of the oxidant and formed elemental sulfur and the corresponding 5,6-carbonates. Adley *et al.*[17] found that cyclic mono- and di-thiocarbonates react with one mole of LT to give the corresponding carbonates, while tri-thiocarbonates afford oxythiocarbonyl compounds under the same conditions. For these transformations the following mechanisms were proposed (Scheme 4).

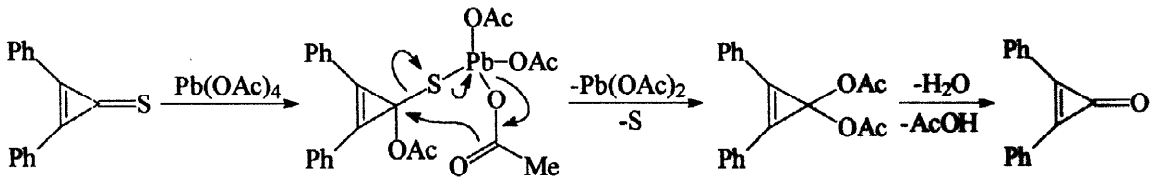


Scheme 4

In the case of mono- or di-thiocarbonates the acetate ion of LT attacks the thiocarbonyl carbon atom yielding the diacetate precursor of carbonates. In the case of tri-thiocarbonates the acetate ion attacks the

thiocarbonyl sulfur atom with the production of a hypervalent sulfur atom as diacetate sulfuranes which collapse in the oxythiocarbonyl compounds.

The direct oxidation of diphenylcyclopropenethione with LT into the corresponding ketone and elemental sulfur was found by Lown and Maloney,[36] who also proposed the above mechanism for this thiocarbonyl-carbonyl conversion (Scheme 5).



Scheme 5

Clearly, the extent to which the reaction involves the cyclic transition state is uncertain; the reaction mechanism can also proceed by steps.

2.1.5. Ceric ammonium nitrate (CAN)

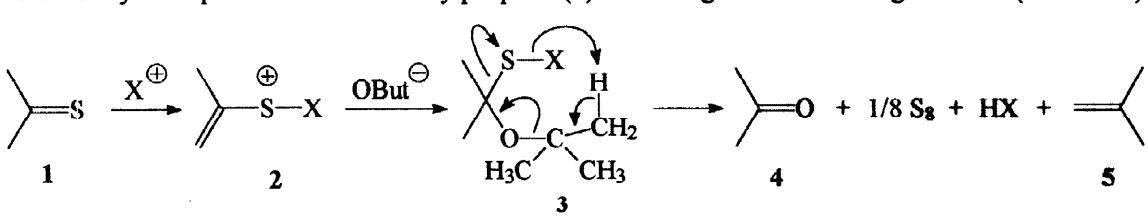
Dhar and Bag[37] have oxidized secondary and tertiary thioamides with CAN to the corresponding amides. On similar oxidation, primary thioamides gave 1,2,4-thiadiazoles.

2.1.6. Copper nitrate (CN) and iron nitrate (IN)

Kristensen *et al.*[38] succeeded in converting secondary and tertiary thioamides into the corresponding amides by the use of CN or IN, but 1,2,4-thiadiazoles were the only products of the same oxidation with primary thioamides.

2.1.7. Hypohalogenites

Reactions with hypohalogenites were used in the past to determine qualitatively and quantitatively thioamides and cyclic and acyclic thioureas. The sulfur atom of the thiocarbonyl group, however, was oxidized to sulfate.[39] More recently, the reaction of *t*-butyl hypochlorite with different thiocarbonyl compounds (secondary and tertiary thioamides, but not primary thioamides which give 1,2,4-thiadiazoles, 2-thiopyrrolidone, several thioureas, thiobarbituric acid, xanthione, thiocoumarin, thiobenzoate and thiocarbonate) was studied by El-Wassimy *et al.*[40] The first step of the reaction is suggested to be the attack of the soft chlorinium ion on the soft sulfur atom of **1** with the formation of an intermediate compound, **2**. The subsequent attack of the *t*-butoxide ion on **2** gives **3**, which undergoes an intramolecular rearrangement to give the carbonyl compound **4** and 2-methylpropene (**5**) according to the following reaction (Scheme 6).

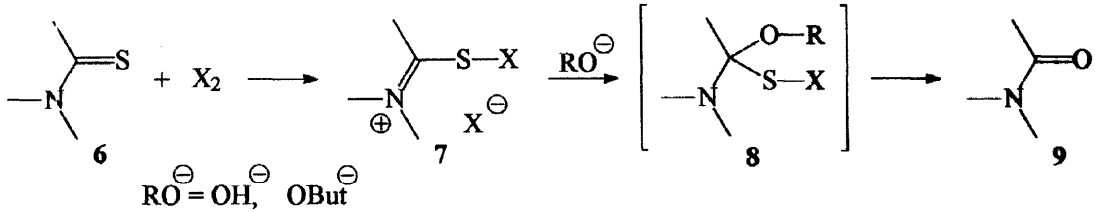


Scheme 6

Analogously, some *p*-acetylbenzenesulfonylurea derivatives were prepared from the corresponding thioureas by treatment with hypohalogenites in the presence of water.[41]

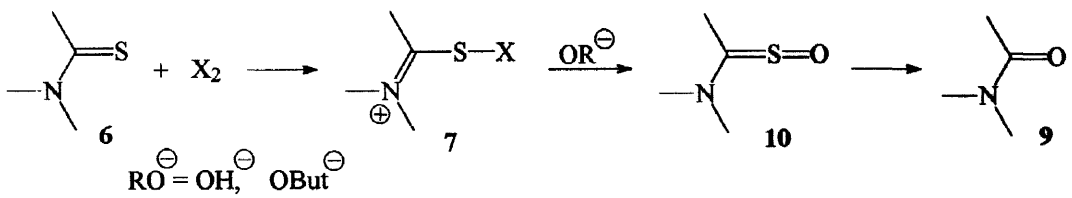
2.1.8. Halogens

Among the different reagents used for >C=S → >C=O conversion, halogens have met with a very high degree of success. The reaction with iodine in alkaline solvents was used for the quantitative determination of thioamides and dithiocarbamic acid derivatives.[42] The reaction between chlorine and some thiocarbonyl sugar derivatives gave the corresponding carbonyl analogues.[43] In the reaction of 1- and 2-naphthylthiourea with bromine Wojahn[44] isolated 2,4-dibromo-1-naphthylurea and 1,6-dibromo-2-naphthylurea, respectively. Singh *et al.*[45, 46] performed the conversion of thioureas, thioamides and thiones into their oxygen analogues by using either (i) potassium *t*-butoxide with iodine, bromine or chlorine, (ii) sodium ethoxide with bromine or chlorine, or (iii) sodium hydroxide with bromine or chlorine under phase transfer catalysis. One of authors[47] of this review almost quantitatively converted N,N-disubstituted thiobenzamide-bromine adducts, generated by adding equimolar amounts of bromine to thioamides in anhydrous solvent at room temperature with hydroxide or *t*-butoxide ions, into the corresponding amides. Sodium methoxide or ethoxide, however, regenerate thiobenzamides. It was suggested that the reaction may be initiated by an attack of the halogen at the sulfur atom of **6** creating an electrophile site at the thiocarbonyl carbon atom of **7** with which the alkoxide or hydroxide ion unites to form the intermediate **8** (Scheme 7). In the case of hydroxide or *t*-butoxide ions the intermediate **8** may undergo a base-induced decomposition to amides **9**, plus sulfur, bromide anion and water or 2-methylpropene as was verified at the time.



Scheme 7

Alternatively, the reaction may involve the initial attack of the oxygen nucleophile of the hydroxide or *t*-butoxide ions at the sulfur atom of the cation **7** which affords the thioamide S-oxide intermediate **10** by deprotonation or elimination of 2-methylpropene. Thioamide S-oxides are known to decompose to amides in these conditions[48] (Scheme 8).

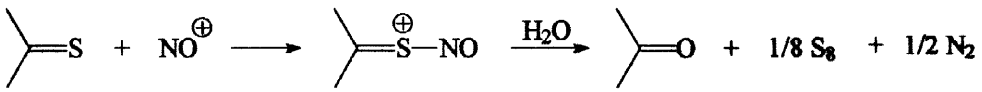


Scheme 8

2.1.9. Nitrosonium ions

Considerable interest has been focused on the >C=S → >C=O oxidation of thiocarbonyl compounds linked to nitrosative exchange. Monosubstituted amides together with sulfides were isolated from a solution of corresponding thioamides in an excess of alkyl nitrite kept at 0°C for two days.[49,50] Jørgensen *et al.*[51] treated thiocarbonyl compounds (secondary and tertiary thioamides, but not primary thioamides which give nitriles, thiolactams, tetrasubstituted thioureas, thioketones, thionocarbonates and thionocarbamates) with sodium nitrite and hydrochloric acid and obtained the corresponding oxo-analogues. The formation of carbonyl

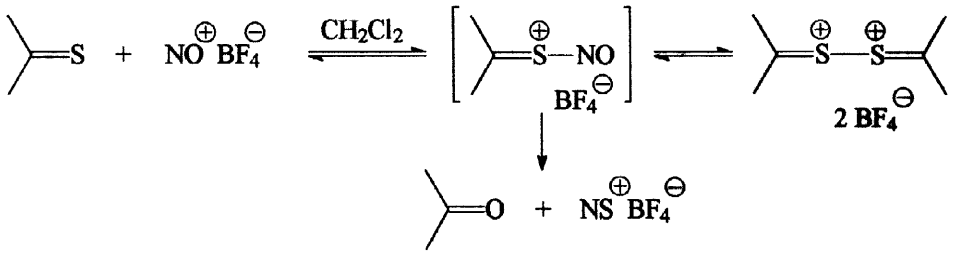
compounds was accounted for by the HSAB principle.[52] The soft acid $NO^{\oplus}$ attacks the soft sulfur atom of the thiocarbonyl compound with the initial formation of a yellow coloured S-nitroso intermediate,[53] which can be detected by UV and ^{15}N NMR spectroscopy.[54,55] The S-nitroso thiocarbonyl compound is hydrolyzed by the water and the carbonyl compound is formed together with elemental sulfur (Scheme 9).



Scheme 9

The kinetics of this reaction were studied by Jørgensen and Lawesson[56] with N-methyl-2-thiopyrrolidone as a model substrate and the reaction was found to be pseudo-first order and proportional to the Pearson's nucleophilicity parameter.[57]

However, the above method is not clean and requires aqueous acidic conditions with an excess of reagents, which is frequently not advantageous. Olah *et al.*[58] and Doyle and Hedstrand[59] used the readily available nitrosomium tetrafluoroborate which proved to work very well under mild conditions. With a tenth molar excess of the reagent at room temperature in dichloromethane solution thioketones, thioamides and 1,3-dithiolane-2-thiones were easily converted in the corresponding oxo-analogues (Scheme 10).



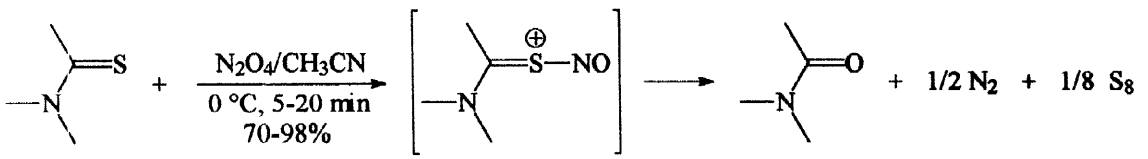
Scheme 10

This reaction involves both the reversible formation of the dithiocarbodication as well as the formation of the carbonyl compound by oxygen-sulfur exchange.

In the presence of nitric oxide a substantial increase in the yield of the carbonyl compound was observed.[59]

Nitrosation of thiocarbonyl compounds was also achieved by Jørgensen *et al.*[60] using N-nitrosoamines (N-nitrosopiperidine and N-nitroso-N-methylaniline) in aqueous acidic solution in the presence of iodine anions. This method transformed secondary and tertiary thioamides, xanthione, thio- and dithiobutyrolactone, thiocoumarin, certain thioureas, and dithio-O,O-thiocarbonic, S,S-trithiocarbonic and N,N-disubstituted thiocarbamic esters.

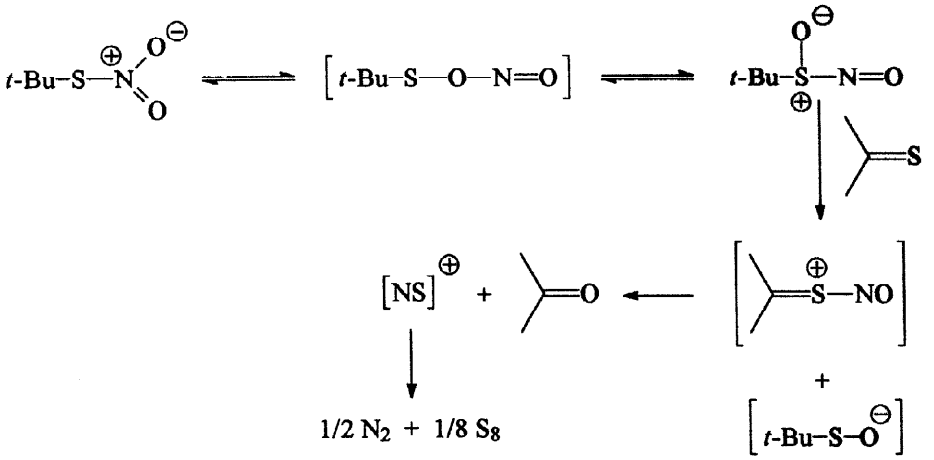
Kim and Kim[61] used dinitrogen tetroxide, which is in equilibrium with nitrosonium cations and nitrate anions, to convert secondary and tertiary thioamides and thionocarbonates into the corresponding oxygen analogues (Scheme 11).



Scheme 11

Furthermore they found that thiocarbonyl compounds, such as thioamides, tri-, di- and mono-thiocarbamates and thioketones, are readily converted into their carbonyl compounds with *t*-butyl thionitrate at 0°C in

acetonitrile.[62] Thionitrate was demonstrated to be a good nitrosation reagent; it is stable at ether reflux temperature, but it is in equilibrium with a rearranged form able to attack the thiocarbonyl group to give the S-nitroso intermediate (Scheme 12).



Scheme 12

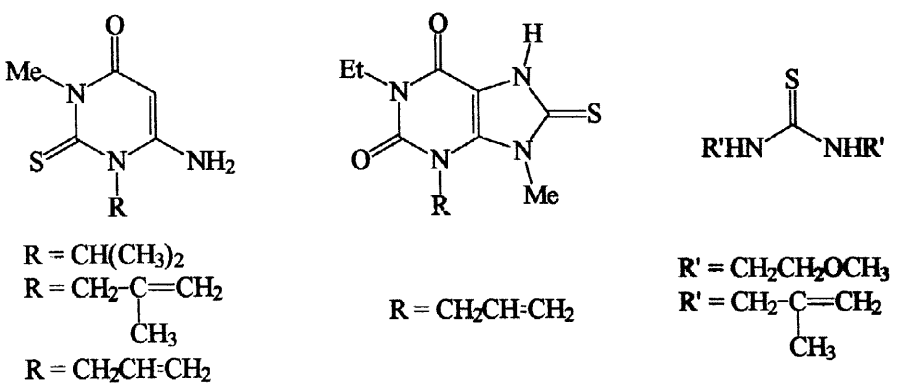
2.1.10. Nitric acid (NA)

In early works Husemann[63] described the reaction of NA with ethylene trithiocarbonate to give the dithiocarbonate, and Losanitch[64,65]described the reaction with diphenylthiourea which also undergoes nitration more than desulfurization yielding tetranitrodiphenylurea. The method involving NA was also used to convert imidazole-2-thiones into imidazole-2-ones[66,67]and cyclohexene trithiocarbonate into the dithiocarbonate.[68]

3. PEROXIDIC REAGENTS

3.1 Alkaline peroxides

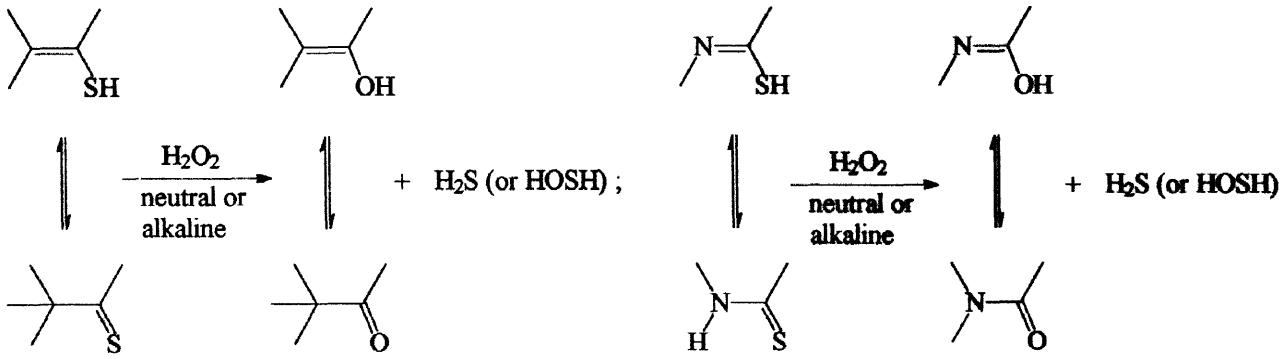
Thioureas were the object of alkaline peroxide oxidation in the works of Vanino and Schinner[69] and Kitamura.[70,71] Their conversion into ureas, however, proved to be inferior to that with hydrogen peroxide.[69-71] Loh and Dehn[2] smoothly oxidized thiocarbanilide with sodium peroxide (SP) in an alkaline medium to give diphenylurea and sulfate. Kalm[72] found that SP oxidation of acyclic and cyclic thioureas was efficient, but it was not preferable to that with hydrogen peroxide only because the handling of large quantities of SP provided some problems in the isolation of ureas from reaction mixtures (Scheme 13).



Scheme 13

3.2. Hydrogen peroxide (HP)

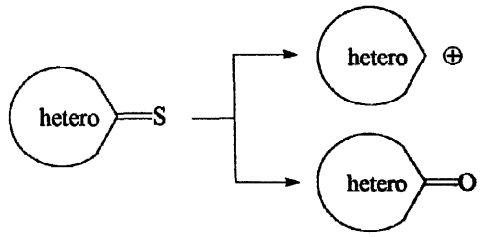
The treatment of acyclic, cyclic and heterocyclic thioketones and thioamides with HP in neutral or alkaline media normally gave only the corresponding ketones and amides[73] (Scheme 14).



Scheme 14

Particularly with heterocyclic thiones the conversion of the thiocarbonyl moiety into the carbonyl moiety concerned the monothio-succinimide and -phtalimide,[74] pyrane-2-thiones,[75] benzo-1,3-oxazine-2-thiones,[76] benzo-3,1-oxazine-2-thiones,[70] thiazolidine-4-thiones,[77,78] benzothiazoline-2-thiones,[79,80] benzo-3,1-thiazine-2-thiones,[70] 1,3-thiazolidine-4-thiones,[81] imidazoline-5-thiones,[82-84] pyrazoline-3-thiones,[71,85] 4,1,2-oxa(thia)diazoline-3-thiones,[83] 1,2,3-thiazine-4-thiones[86] and 5-aryl-1,1-dioxo-5,6-dihydro-1,4,2-dithiazine-3-thiones.[87]

The treatment of a variety of heterocyclic thiones with HP in acetic acid produces either heteroaromatic cations or the corresponding oxo-compounds. The results may be correlated with structural and electron features. Benzo substrates or the presence of strongly electron withdrawing groups in the molecule favours the formation of oxo-compounds, whereas the presence of a σ-trivalent nitrogen atom favours aromatic cations (Scheme 15). Thus only 1,2,4-dithiazoline-3-thiones,[88] pyran-2-[89,90] and 4-thiones,[89,91] thiopyran-2-[89,92] and 4-thiones,[89] benzoxazole-2-thiones,[93] imidazolopyrimidine-4-thiones,[94] and 6-methyl-2-thiouracil[70] give the corresponding ketones.



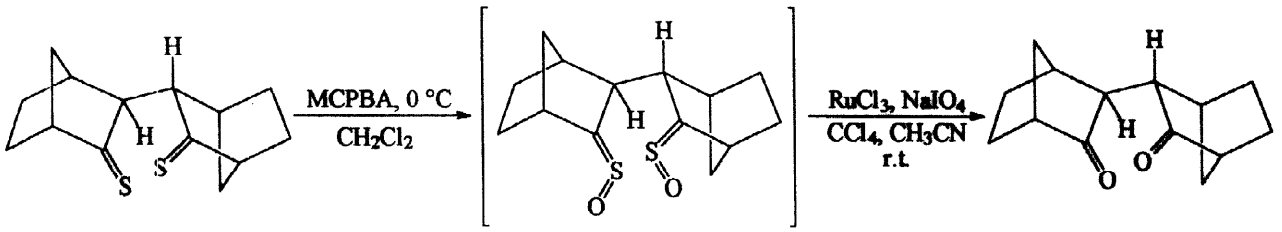
Scheme 15

Thiourethanes and trithiocarbonates were oxidized with HP in neutral or acid media into the corresponding S-oxides.[95] The latter, however, are more or less stable and finally give ketones.[96]

3.3 Peroxyacids

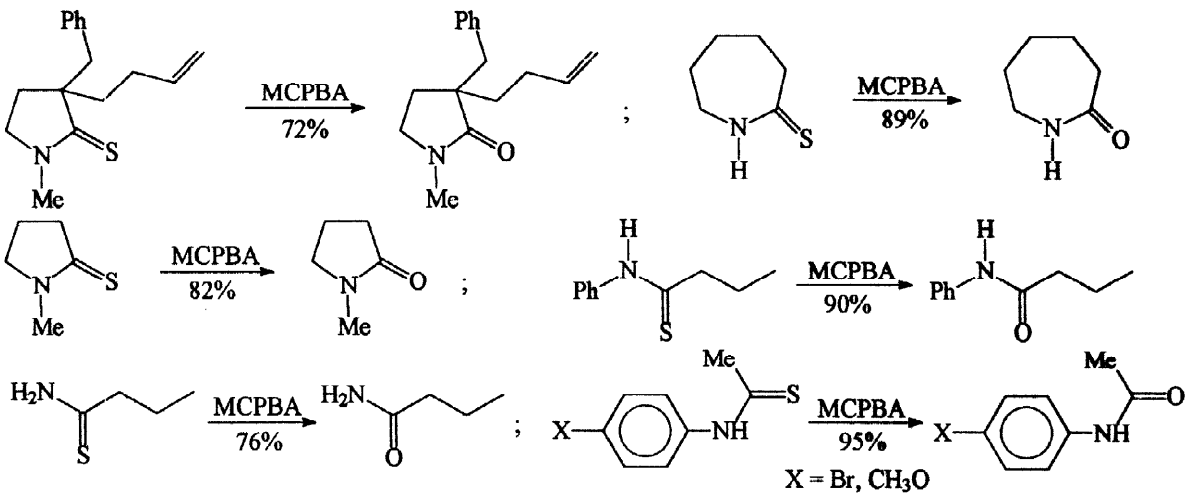
Generally, oxidation with peroxyacids converts the thiocarbonyl (>C=S) group into the sulfine (>C=S=O) bond,[96] but this then reacts further, albeit much more slowly, to give the >C=O double bond together with sulfur and sulfur dioxide.

For example, in a study, on the oxidation of the bithiocamphor Le Corrè *et al.*[97] succeeded in oxidizing it into the corresponding disulfine with *m*-chloroperbenzoic acid (MCPBA) according to Metzner's conditions[98,99] and then transformed it into the diketone using ruthenium trichloride and sodium periodate (Scheme 16).



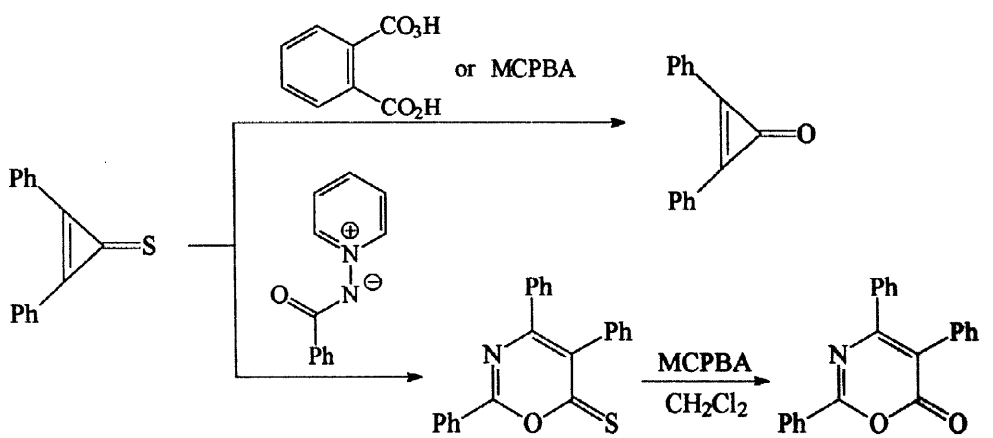
Scheme 16

In connection with a total synthesis of alkaloids, Pinnick *et al.*[100] found that the conversion of thioamides as well as thiolactams into amides and lactams with MCPBA proceeds with high yields and that primary, secondary and tertiary thioamides undergo this reaction with equal efficiency (Scheme 17).



Scheme 17

In oxidation experiments performed on diphenylcyclopropenethione with MCPBA or monoperphthalic acid Lown and Maloney[36] observed that the final reaction product was diphenylcyclopropenone and they confirmed the structure of 1,3-oxazine-6-thione, obtained by reaction of diphenylcyclopropenethione with N-substituted pyridinium imines, by reaction with MCPBA which afforded the corresponding ketone (Scheme 18).[101] Similarly, thiopyran-4-thione[102] and 1,3-dithiole-2-thione[17] derivatives were oxidized into the corresponding oxygen analogues.



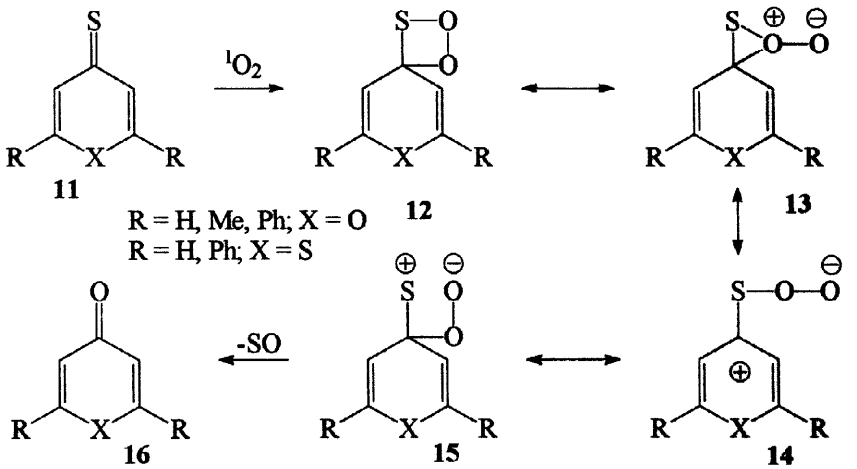
Scheme 18

In several cases, however, the oxidation of thioketones with peroxyacids leads to the corresponding ketones.[103]

4. MOLECULAR OXYGEN

Molecular oxygen has been recognized to be a good electrophile[104] able to accomplish the conversion of thiocarbonyl compounds into carbonyl compounds by irradiation.

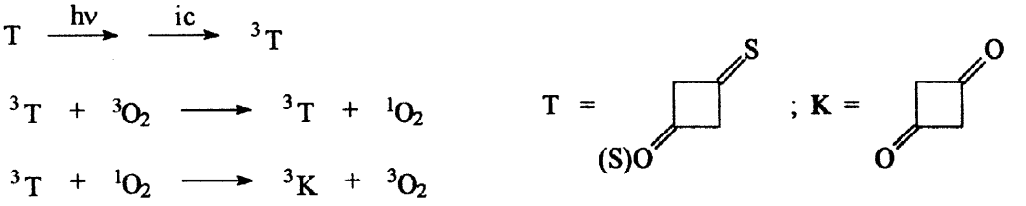
The stability of several thioketones toward oxygen with or without irradiation has been known for a long time,[105-109] and in every case the corresponding ketones have been the reaction products, but neither the mechanism nor the reactive species involved in these reactions have been established. Ishibe *et al.*[110,111] were the first to describe the characterization of products and the mechanism of the dye sensitized photo-oxygenation of 4H-pyran-4-thiones and 4H-thiopyran-4-thiones **11** (Scheme 19).



Scheme 19

Photo-products were the corresponding ketones **16** and yields were in the range 50-70%. The quenching of the oxygenation by carotene suggested that the reactive species is the singlet oxygen which adds to thioketones **11** to form intermediates **12** for which alternative structures **13**, **14** and **15** are possible. The rupture of the C-S bond in these intermediates, followed by the elimination of sulfur monoxide results in the formation of ketones **16**

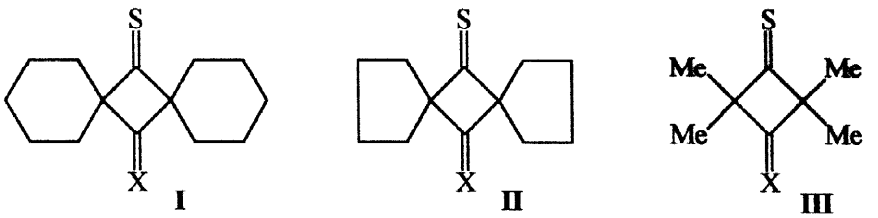
Worman *et al.*[112] irradiated tetramethyl 1,3-cyclobutanedione-3-thione and -1,3-dithione in the presence of oxygen in isopropyl alchohol at wave lengths of 400 nm and obtained the diketone. They suggested that the excited state of the thione itself photosensitizes the formation of singlet oxygen from triplet oxygen. Singlet oxygen then reacts with the ground state of the thione to give the cyclic intermediate which collapses to give the product (Scheme 20).



Scheme 20

Ramamurthy and Sundari[113] conducted direct and methylene blue-sensitized photo-oxygenation and singlet oxygen oxidation of a series of 1,3-cyclobutanedione-3-thione and -1,3-thiones (**I**, **II**, and **III**), which

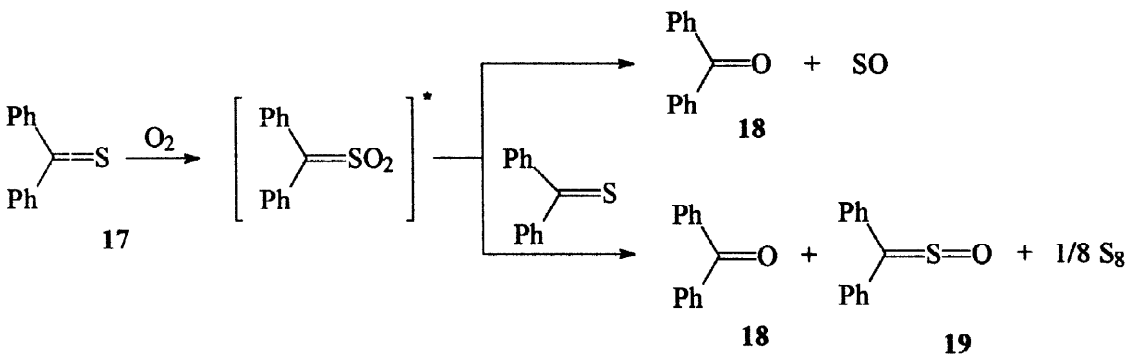
gave corresponding sulfines and/or ketones. The product distributions from **I**, **II** and **III** are due to electronic and steric substituent effects on the zwitterionic peroxide formed from the interaction of singlet oxygen with the chromophore (Scheme 21).



X (I, II, III) = O, S

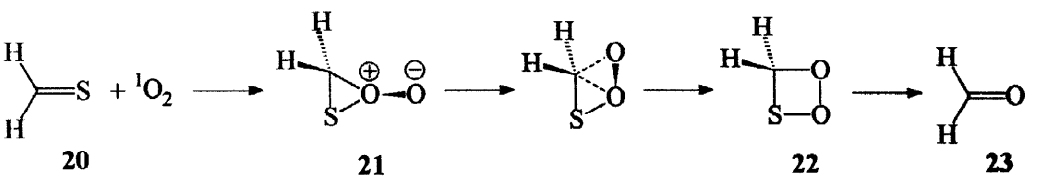
Scheme 21

Carlsen[114] studied the reaction of thiobenzophenone **17** with oxygen in the dark in different solvents and found that benzophenone **18**, and thiobenzophenone S-oxide **19**, together with sulfur and sulfur dioxide, are the reaction products. He observed that the reaction rate between thioketone **17** and oxygen was highly solvent dependent although the product ratio of **18** to **19** was found to be nearly constant (ca. 0.8), and rationalized the reaction mechanism as in Scheme 22.



Scheme 22

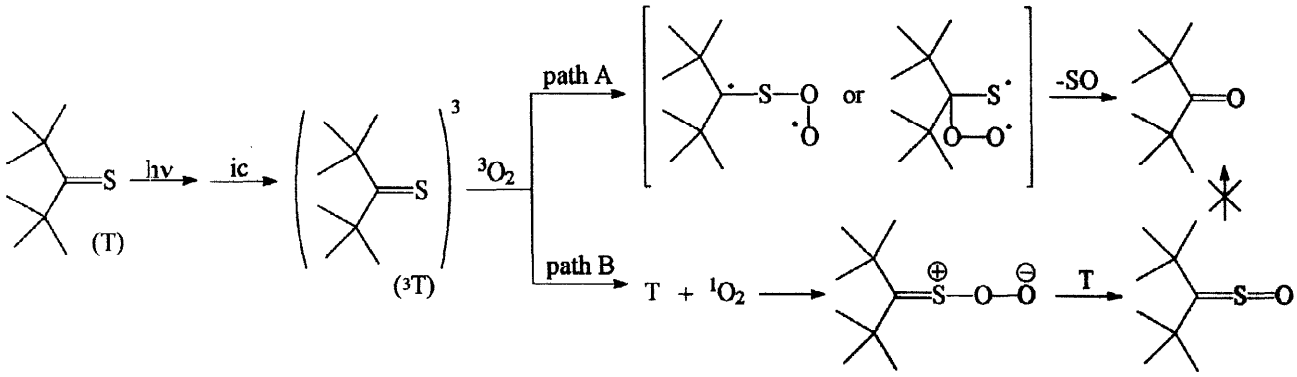
Carlsen[115] also investigated theoretically the reaction between thioformaldehyde and singlet oxygen with a CNDO/B framework. Based on potential energy surface calculations he predicted a multistep mechanism involving primary formation of an oxathiirane O-oxide **21**, which rearranges into a 1,2,3-dioxathiethane system **22**. This latter four-membered ring, by analogy with the dioxethane system,[116] was tentatively suggested to decompose *via* a biradical-type intermediate into formaldehyde **23** (Scheme 23).



Scheme 23

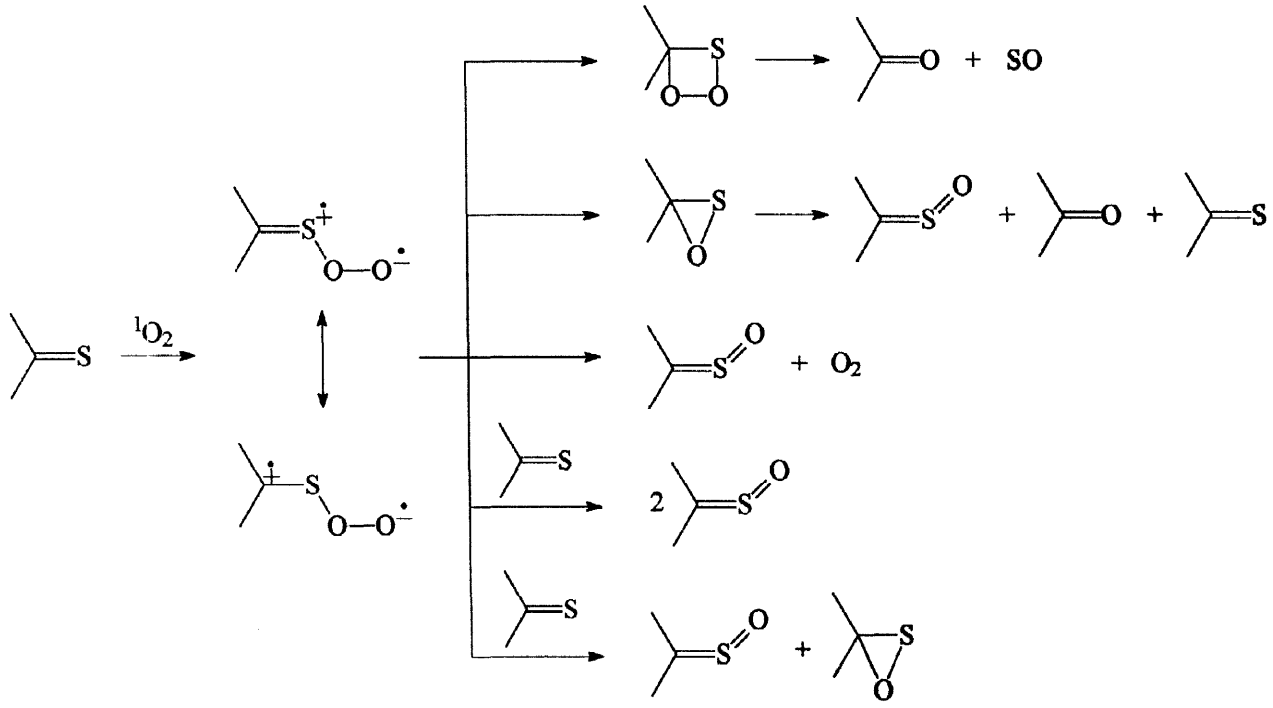
Tamagaki *et al.*,[117] based on the photo-oxidation of di-*t*-butyl thioketone, pointed out that there are two different reaction paths leading to the ketone and sulfine. The former (path A) is probably produced through a short-lived biradical-type intermediate which is formed by the direct interaction of the triplet thioketone with

molecular oxygen in the ground state, while the latter (path B) is indeed produced by the oxidation with singlet oxygen. Later on, they studied the singlet oxygenation of 1,2-benzodithiole-3-thione and found that the reaction proceeds *via* a sulfine, but not *via* a dioxathiethane intermediate (Scheme 24).[118]



Scheme 24

Ramamurthy *et al.*[119-124] carried out a systematic investigation on the oxidation of a variety of aromatic and aliphatic thiones by singlet oxygen generated *via* self-sensitization and by other independent methods which yielded the corresponding ketones with or without sulfines in varying amounts. He believed that a zwitterionic/diradical intermediate arising out of the primary interaction of singlet oxygen with the thiocarbonyl chromophore is the common intermediate for the ketone and sulfine. The closure of the zwitterionic/diradical intermerdiate affords 1,2,3-dioxathiethane which leads to the ketone, while the competing oxygen elimination leads to the sulfine. This partitioning is governed by steric and electronic factors operating on the zwitterionic/diradical intermediate (Scheme 25).



Scheme 25

Ramamurthy *et al.*[125] also studied the photo-oxidation of α,β-unsaturated thiones, which yield the corresponding ketones as the only products. He suggested that the thiocarbonyl chromophore is the site of attack by singlet oxygen and that the adjacent carbon-carbon double bond is inert under these conditions. The absence of sulfine during the oxidation of α,β-unsaturated thiones is attributed to the electronic factors operating on the zwitterionic/diradical intermediate.

Quite interestingly, he carried out the photochemical oxidation of eleven diaryl thioketones in the solid state. Only six ketones were oxidized to the corresponding carbonyl compounds, whereas the rest were photostable.[126] However, in solution all were readily oxidized. The difference in behaviour between thioketones in the solid state and in solution was rationalized on the basis of molecular arrangement in the crystal.

Gano and Atik[127] photolysed thioesters with a medium pressure mercury lamp in carbon tetrachloride solution through which oxygen was continually bubbled and obtained esters as the sole photo-products. The replacement of sulfur by oxygen in thiocarbonyl compounds appears to proceed by the formation of singlet oxygen (Scheme 26).

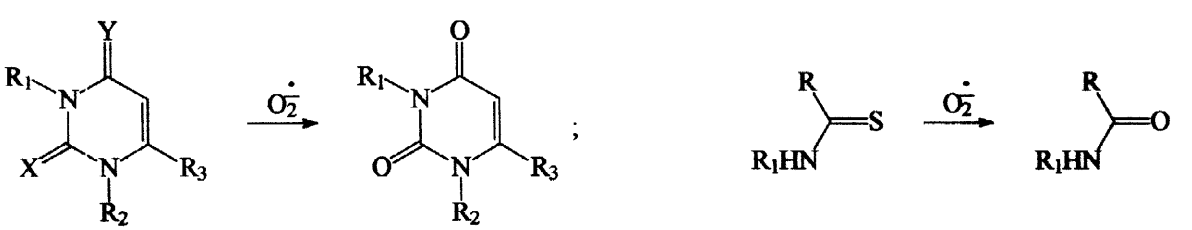
Scheme 26

Photosensitized oxygenation of 10-methyl-9(10H)acridinethione, 9H-xanthene-9-thione, 9H-thioxanthene-9-thione[128,129] and 1,3-thiazin-6-thiones[130] quantitatively afforded the corresponding ketones.

5. SUPEROXIDE ANION

In connection with bioorganic studies on the activation mechanism of molecular oxygen,[131-133] investigations were undertaken to explore the desulfurization of thiocarbonyl compounds by using the superoxide anion[134-137,96] as a model of metabolic reactions.

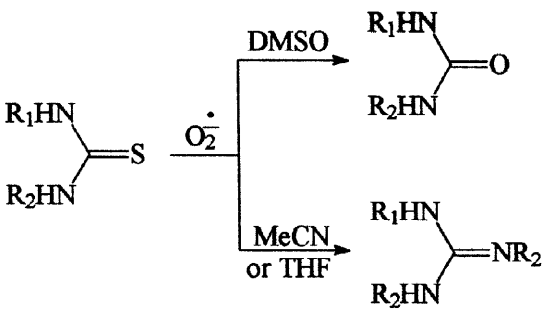
On treatment with the superoxide anion generated by potassium superoxide with catalyst crown ether or by electrolysis of oxygen, Katori *et al.*[134] readily desulfurized cyclic and acyclic thioureas and thioamides within one hour at r. t. in aprotic solvents into the corresponding carbonyl compounds with yields varying from 61 to 88% (Scheme 27).



X = S; Y = O
X = O; Y = S
X = Y = S

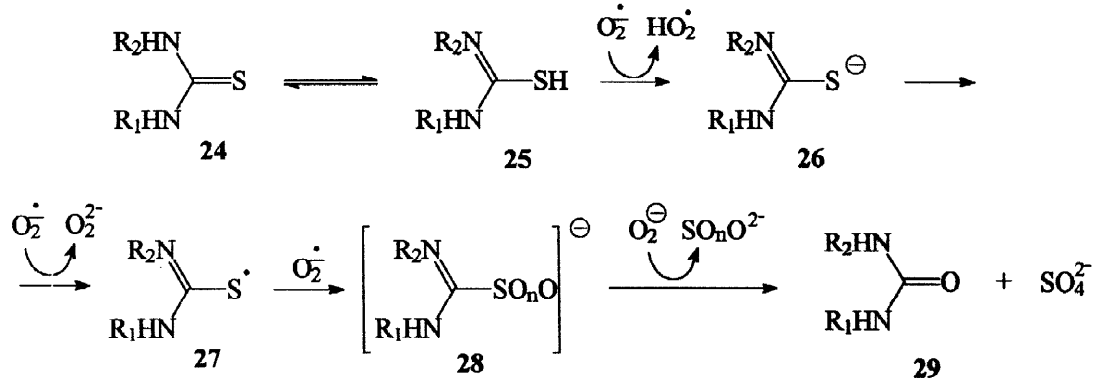
Scheme 27

Kim *et al.*[136,137] found that some 1,3-disubstituted thioureas reacted with the superoxide anion to give a mixture of 1,2,3-trisubstituted guanidines or 1,3-disubstituted ureas and potassium sulfate depending on the solvent used. The main products were guanidines in acetonitrile or tetrahydrofuran and ureas in anhydrous dimethyl sulfoxide (Scheme 28).



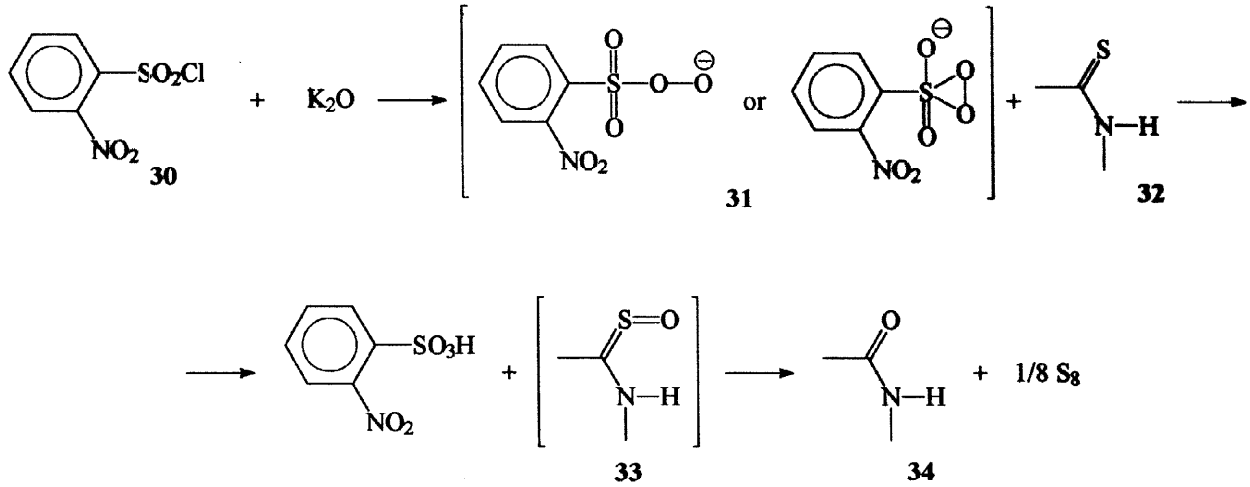
Scheme 28

No oxidation product occurred with tetrasubstituted thioureas. Thus the oxidation appears to require at least one proton which is necessary for the tautomeric change from the thiourea **24** to the thiol form **25**. In the presence of the superoxide anion the thiol **25** is converted in the thiolate anion **26** and transformed into the thiyl radical **27** by one electron transfer. This radical couples with the superoxide anion to form peroxysulfenate **28** or its functional equivalents (peroxysulfinate or peroxysulfonate), which gives urea **29** and sulfate in the alkaline medium (Scheme 29).



Scheme 29

In contrast with these results, the desulfurization of thioamides **32** with the superoxide anion in the presence of 2-nitrobenzenesulfonyl chloride[137] **30** at ca. -35°C under dry argon atmosphere results in a clean and quantitative conversion into their corresponding amides **34**. In this case the desulfurization proceeds with a different mechanism, which initiates the oxidation of the thioamide **30** into the sulfine **33** *via* a peroxysulfur intermediate **31** formed by nucleophilic attack of the superoxide anion on the sulfonyl sulfur of **30**. The sulfine **33** may quickly convert into the carbonyl compound **34** as in the case of the oxidation of thiones to ketones through sulfine intermediates (Scheme 30).[96]

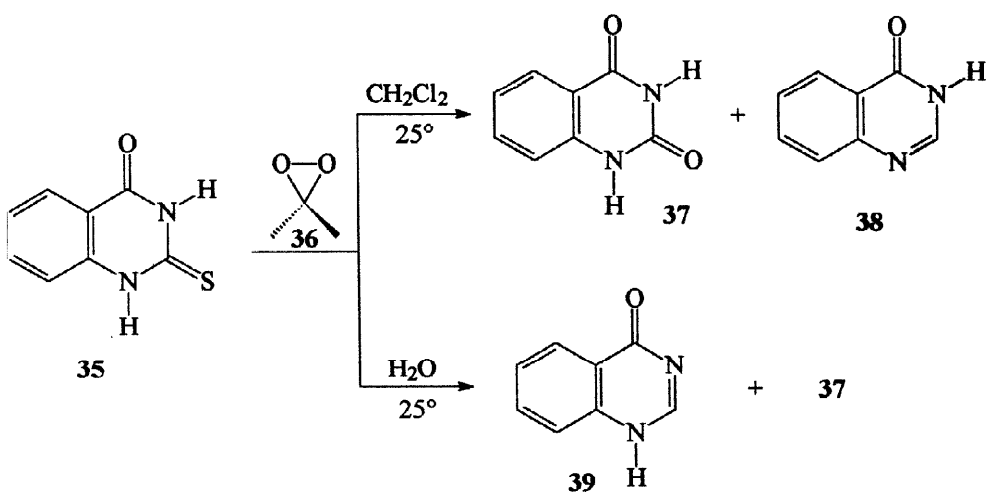


Scheme 30

6. DIMETHYL DIOXIRANE

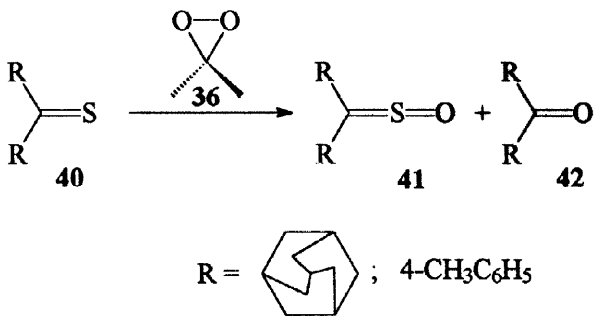
Dioxiranes proved to be useful reagents to convert the thioamide moiety of pyrimidine derivatives into the amide group, but they gave also other products of oxidative desulfuration.[138,139]

Saladino *et al.*[138] obtained 2,4(1H,3H)-quinazolindione **37** along with 4(3H)-quinazolinone **38** by treatment of the corresponding 2-mercapto-4(3H)-quinazolinone **35** with a freshly prepared solution of 3,3-dimethyl-1,2-dioxirane **36** in dichloromethane at 25°C. When water was used as the solvent, 4(1H)-quinazolinone **39** together with **37** were obtained (Scheme 31).



Scheme 31

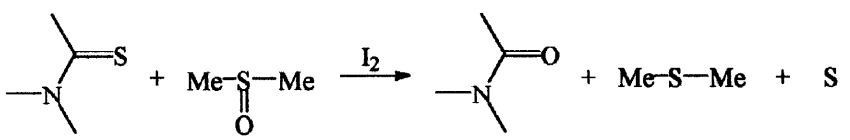
In the reaction of thioketones **40** with dimethyl dioxirane Tabuchi *et al.*[139] obtained ketones **42** as secondary products together with the thione-S-oxides **41** (Scheme 32).



Scheme 32

7. DIMETHYL SULFOXIDE

Mikolajczyk *et al.*[140-143] and Kinoshita *et al.*[144,145] treated thioureas, thionocarbamates and thiouracils with dimethyl sulfoxide in the presence of an electrophile such as sulforic acid, boron trifluoride or iodine to give the corresponding ureas, carbamates and uracils. Other secondary products were dimethyl sulfide and sulfur (Scheme 33)



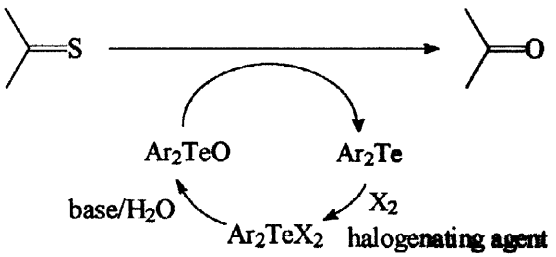
Scheme 33

The activation of dimethyl sulfoxide by iodine through the charge-transfer complex **43** or sulfoxonium salt **44** needs further study (Scheme 34).

Scheme 34

8. TELLURIUM OXIDES

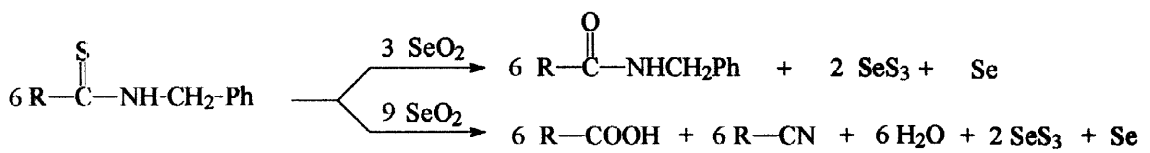
Bis(4-methoxyphenyl) telluroxide, which is prepared by basic hydrolysis of the corresponding diaryltellurium dichloride,[146] is a mild and highly selective oxidizing reagent for the conversion of thiocarbonyl compounds into their corresponding oxo-analogues.[147] By-products of the reaction were sulfur and diaryltelluride, which could be reoxidized to telluroxide using 1,2-dibromotetrachloroethane and aqueous potassium carbonate.[148] Telluroxide has been shown to react with xanthates, thiocarbonates, thiobenzoates, thioamides and thiones in chloroform or dichloromethane at room temperature under a nitrogen atmosphere to give the corresponding carbonyl compounds (Scheme 35). The enolizable thiocamphor gave a mixture of products consisting of two divinyl disulfides (67%) and camphor (10%).



Scheme 35

9. SELENIUM OXIDES

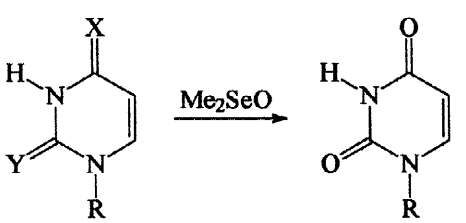
The employment of selenic derivatives represents a mild method which compares favourably with other literature processes. Boudet[149-152] was the first to use selenium dioxide to convert benzylthioamides into benzylamides with almost quantitative yields by using a stoichiometric ratio of SeO_2:thioamide (= 1:2). It was proved that by using an excess of selenium dioxide (SeO_2:thioamide ratio = 3:2) the molecule of thioamide undergoes an oxidative degradation to give benzonitrile and the acid corresponding to the thioamide (Scheme 36).



Scheme 36

Tamagaki *et al.*[153] reacted diphenyl and dibenzyl selenoxides with equimolar amounts of thiolactams and cyclic thioureas to give the corresponding oxygen analogues, selenides and sulfur.

Dimethyl selenoxide was found by Mikolajczyk and Luckak[154] to be an excellent agent which converts various thiocarbonyl compounds into their carbonyl analogues under very mild conditions in the absence of a catalyst. For this reason dimethyl selenoxide has been indicated as a reagent of choice for selective modification of the thiocarbonyl containing minor components of transfer ribonucleic acids (Scheme 37).



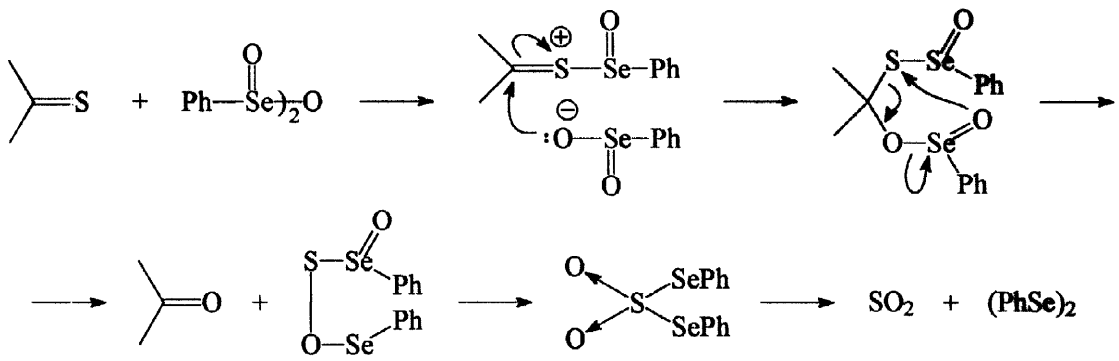
a, Y = S; X = O; R = H
b, Y = O; X = S; R = H
c, T = S; X = O; R = H
d, Y = O; X = S; R = ribofuranosyl

a, R = H
b, R = ribofuranosyl

Scheme 37

Barton *et al.*[155,156] converted a number of xanthates, thioesters, thiocarbonates, thioamides and thiones into the parent carbonyl derivatives in high yields by treating them with benzeneselenic anhydride at room

temperature in tetrahydrofuran. A limitation was found with thiocarbonyl compounds which undergo a facile enolisation. Evidence was obtained for the mechanism outlined in the Scheme 38.

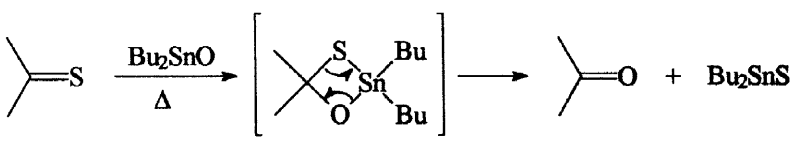


Scheme 38

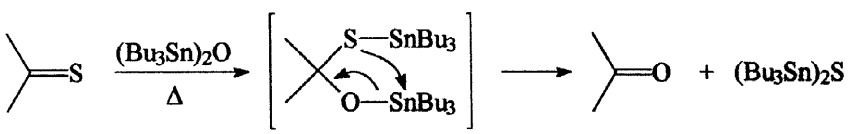
10. TIN OXIDES

Tsuda *et al.*[157] used dibutyltin oxide (method A, Scheme 39) or bis-tributyltin oxide (method B, Scheme 39) to convert cyclic thionocarbonates derived from carbohydrates and thionolactones into the corresponding carbonates and lactones, respectively, by both methods A and B. Cyclic thionocarbonates derived from alditols gave the expected oxo-products in acceptable yields by method B, and tertiary thiolactones gave the corresponding lactams only by method A in low yield with considerable recovery of the starting materials.

Method A



Method B



Scheme 39

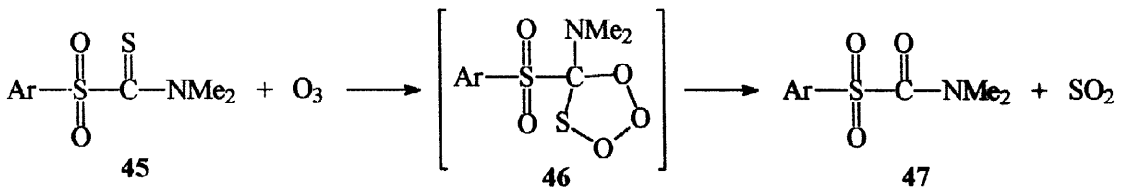
The proposed mechanism foresees that the borderline soft tin species attacks the soft sulfur atom of the thiocarbonyl group to give an intermediate which produces the carbonyl compound because of its O–S exchange process. Thioamides or thioureas are affected very slowly if at all.

11. 1,3-DIPOLAR CYCLOADDITIONS

1,3-Dipoles containing an oxygen atom in the terminal position seem to be good reagents for the >C=S → >C=O conversion since their cycloadducts with the >C=S double bond are unstable and decompose to give the >C=O double bond.

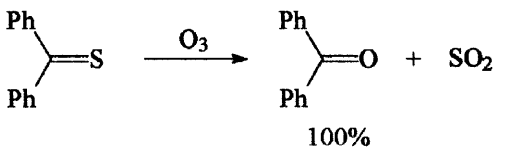
11.1. Ozone

A few reports have appeared on the ozonolysis of thiocarbonyl compounds and the results of these ozonolysis reactions seldom see the ozone as a 1,3-dipolar system, and only rarely as an electrophilic reagent. In a Russian work it was reported that tri-*n*-butylthiourea reacts with ozone to give a mixture of tri-*n*-butylurea and *n*-butylisocyanate.[158] Senning *et al.*[159-161] reported the ozonolysis of C-sulfonylthioformamides **45**, which lead to the C-sulfonylformamides **47** and assumed that the ozone attacks the carbon-sulfur double bond in a 1,3-dipolar cycloaddition forming the intermediate **46**, which subsequently decomposes to **47** and sulfur dioxide (Scheme 40) and their reaction generally takes place under mild conditions.



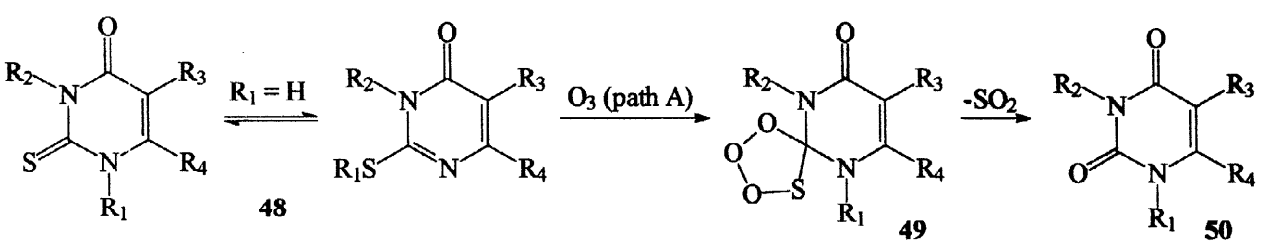
Scheme 40

Zwanenburg and Janssen[162] investigated the reaction between diaryl thioketones and ozone in an attempt to synthesize the corresponding sulfines. While a partial formation of sulfines is observed with sterically hindered thioketones, unhindered thioketones, such as thiobenzophenone, give rise only to the corresponding ketones (Scheme 41).



Scheme 41

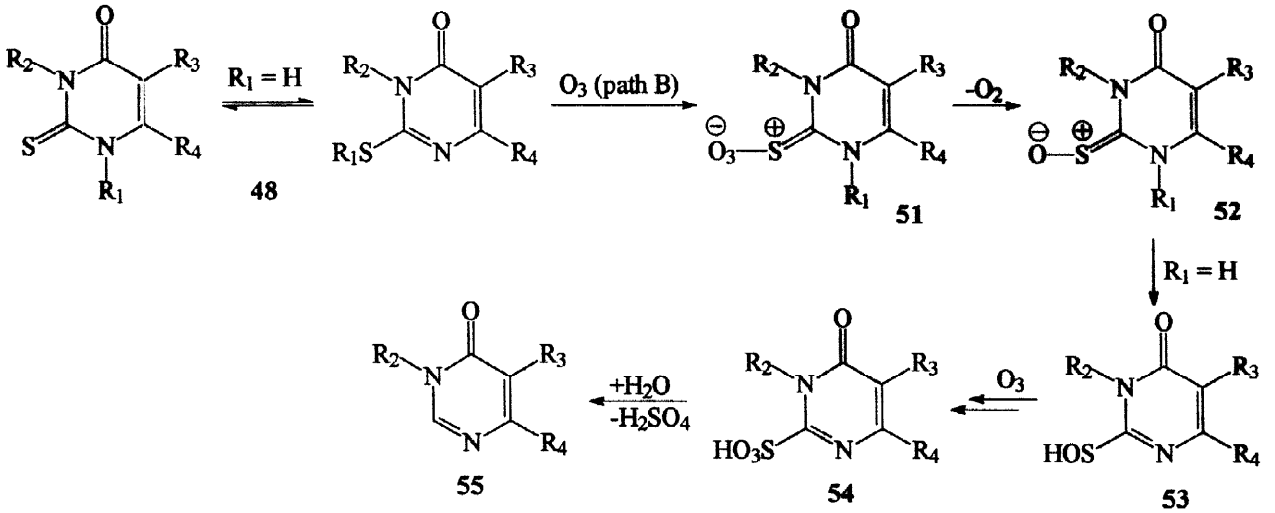
A similar reaction has been reported by Matsui *et al.*[163] who ozonized 2-thiouracils **48** to obtain the corresponding uracils **50** and 4(3H)-pyrimidones **55**. They proposed that, the thiocarbonyl moiety may undergo a 1,3-dipolar cycloaddition, to give an adduct **49** from which the carbonyl compound **50** is obtained by extrusion of sulfur dioxide (Scheme 42, path A).



Scheme 42

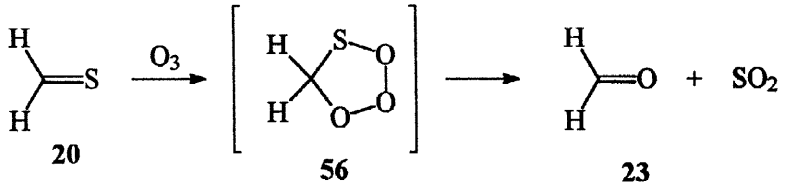
Alternatively the thiocarbonyl group may undergo (Scheme 43, path B) an electrophilic attack on the sulfur atom to give the ozone-adduct **51** which gives the sulfine **52** by deoxygenation. From the sulfine **52**, uracils **50** and pyrimidones **55** can be obtained. The latter in particular derives from **52**, which is in equilibrium

with the sulfenic acid **53** for R_1 = H, by further oxidation to sulfonic acid **54**. Finally, the water contained in the solvent desulfurized **54** to **55**.



Scheme 43

From his theoretical studies on the model reaction between thioformamide **20** and ozone by a CNDO/B procedure, Carlsen[164] proposed that a structure of type **56** is a possible intermediate in this ozonization (Scheme 44).

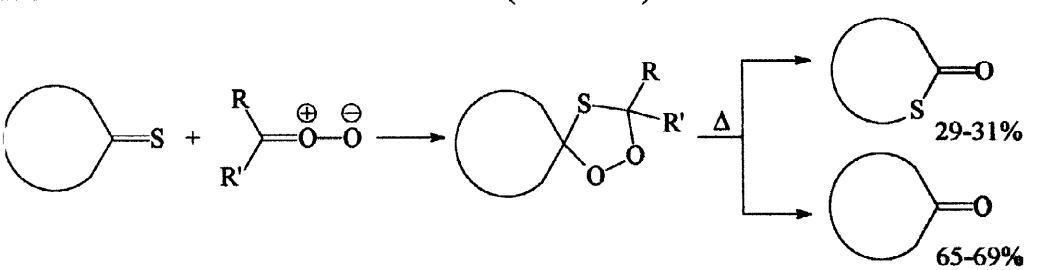


Scheme 44

Nicoletti *et al.*[138,165] showed that the ozonolysis of substituted 2-thiouracils and pyrimidine-2-thiones gives the oxygen analogues as the main products when water is used as cosolvent.

11.2. Carbonyl oxides

Ozonolysis of vinyl ethers is the method by which carbonyl oxides are generated and are open to undergo 1,3-dipolar cycloaddition reactions. Among various dipolarophiles, thiones add carbonyl oxides to give thiozonides which afford mainly the corresponding ketones by thermolysis. Nojima *et al.*[139,166] treated a solution of vinyl ether and bulky thiones in diethyl ether or methylene chloride with ozone at -70°C and obtained thiozonides in moderate to low yields. The thermolysis of thiozonides in refluxing *t*-butylbenzene led to the formation of a mixture of thioesters and ketones (Scheme 45).



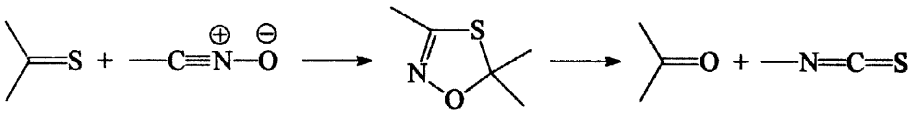
Scheme 45

Diaryl thioketones directly afford thione S-oxides and ketones probably because the nucleophilic oxygen transfer reagent of carbonyl oxides attacks preferentially at the terminal sulfur atom.

11.3 Nitrile oxides

The C=S double bond of several thiocarbonyl derivatives such as thioketones,[167-173] thionocarboxylates,[167,174] dithiocarboxylates,[168,172] trithiocarbonates,[168,172] thioamides,[167] thionocarbonates,[168] thioureas,[167] thioketenes,[174-176] N-thioaroyl-N,N-dimethylformamidines,[177] cyanothioformamides,[178] trithiocarbonate-S,S-dioxides,[179] 1,2,4,5-tetrazinon-2-thiones,[180] 1,2-dithiole-3-thiones,[181,182] 3-aryl-1,4,2-dithiazoline-5-thiones,[183] carbon disulfide,[184] imidazole-2-thiones,[185] 4,1,2-oxa(thia)diazoline-3-thiones[185] and 1,2,4-triazine-3-thiones[185] proved to be reactive towards nitrile oxides.

1,4,2-Oxathiazoline cycloadducts are more or less thermally stable and decompose to give isothiocyanates and the corresponding carbonyl compounds (Scheme 46).



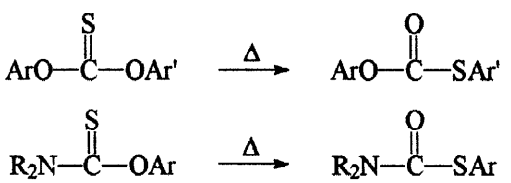
Scheme 46

Depending upon the nature of the thiocarbonyl compounds, decomposition occurs even at low temperature, as for example in the case of thioamides, and only the decomposition oxo-products are obtained.

From kinetic studies Dondoni *et al.*[169] suggested that the reaction of nitrile oxides and thiobenzophenone is a concerted process as predicted by orbital symmetry selection rules for 1,3-dipolar cycloadditions.

12. THERMAL REARRANGEMENTS

The thermal thiono-thiolo rearrangement which occurs in thionocarbonates of Schönberg *et al.*[186,187] and in thiocarbamates of Araki *et al.*[188,189] can be considered as a >C=S → >C=O conversion, even if this was proved to be useful for the preparation of thiophenols from the corresponding phenols. The conversion was practically quantitative when the thionoester was used as hydrochloride[190] (Scheme 47).



Scheme 47

Kinoshita *et al.*[191] showed that the acid catalyzed rearrangement of a mixture of two thionocarbonates proceeds by an intramolecular alkylation. From kinetic studies this unimolecular[192] rearrangement seems to be initiated by a nucleophilic attack of the thiocarbonyl group on the aromatic ring forming a four membered ring at transition state as shown in Figure 1.

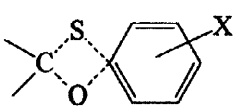
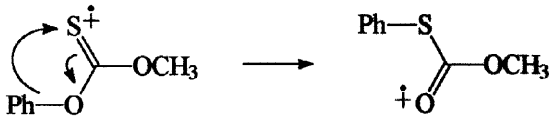


Figure 1

Electron-withdrawing substituents facilitate the reaction.[193]

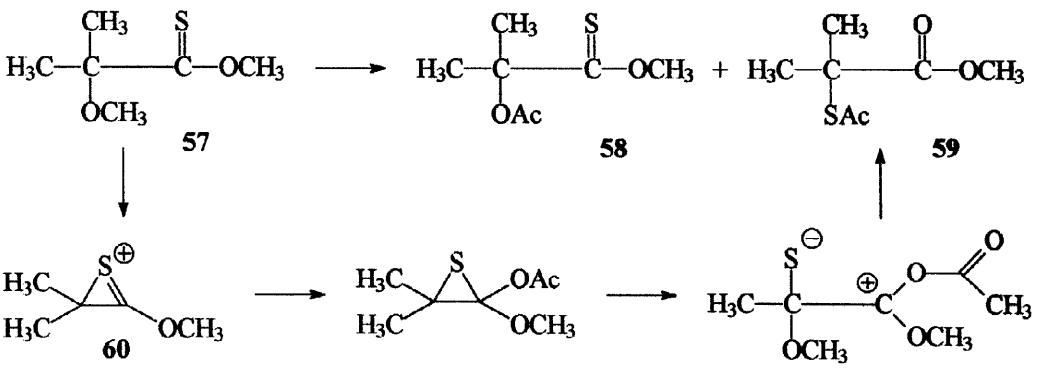
Similar rearrangements were found by Djerassi *et al.*[194] in the electron impact. In this case, however, the most ionizable electron is that of the lone pair on the sulfur atom and the nucleophilic attack of the phenyl group at the sulfur is proposed as driving force of the reaction (Scheme 48).



Scheme 48

Ethylene thionocarbonate and 1,3-oxathiolane-2-thione were isomerized by Jones and Andreades[195] to the thiol- and dithiol-carbonate by the action of potassium iodide at 60°C.

Creary and Mehrsheikh-Mohammadi[196] found that the mesylate derivative of α-hydroxythioester **57** when subjected to acetolysis undergoes a thermal rearrangement which leads to the ester **59**, beside the expected substitution reaction leading to the acetyl derivative **58**. This was explained by the solvent capture at the trigonal carbon atom of **60**, followed by ring opening and acetyl transfer (Scheme 49).



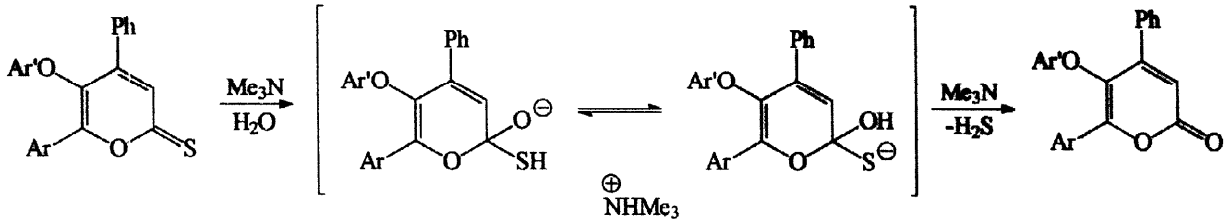
Scheme 49

13. HYDROLYSIS

The direct hydrolysis of thioketones has been observed in boiling water,[197] but alkaline or acid hydrolysis is generally conducted with thiocarbonyl compounds. However, hydrolysis catalyzed by metal ions is preferable, when it is possible, because it is the cleanest.

13.1. Alkaline and acid hydrolysis

According to Mollin and Pavla,[198] the alkaline hydrolysis of benzothioamides predominantly gives the corresponding benzamides and the hydrolysis reaction is first order with respect to the hydroxyl anion in water and second order with respect to hydroxyl anion in 50% aqueous ethanol. The conversion of thioketones, dithioesters, thioamides, and thioureas into the corresponding oxygen analogues with sodium hydroxide under phase transfer conditions can be satisfactorily carried out.[199] Rafla[200] showed that 6-aryl-5-aryloxy-4-phenylpyran-2-thiones undergo hydrolysis to the corresponding oxygen analogues on treatment with aqueous trimethylamine (Scheme 50) and Gompper and Elser[201] produced the same results on treatment with potassium *t*-butoxide.



Scheme 50

Thiocarbonyl compounds are attacked by electrophiles, at least formally, and give rise to complexes which subsequently undergo an easy hydrolysis.[202] Thus, the reaction of dithiepine-5-thiones with sulforic acid resulted in their complete hydrolysis.[203]

13.2. Hydrolysis catalyzed by metal ions

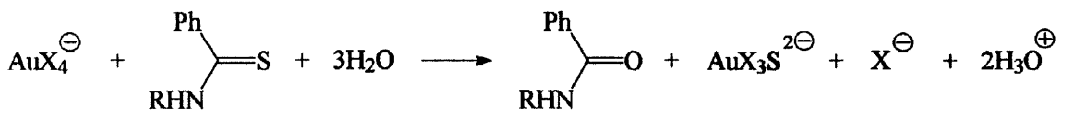
Hydrolysis catalyzed by metal ions, however, has been the most used because the metal ion acts as an electrophile for the sulfur atom of the thiocarbonyl group resulting in weakening of the C-S bond. In some cases the metal ion coordinates to the reagent to form a kinetically active ternary complex. The hydrolysis of thioacetamide in the presence of several metal ions has been extensively studied at different pHs in relation to the precipitation of sulfides by the developed hydrogen sulfide, but the corresponding carbonyl compound has been neglected.

13.2.1. Silver(I) ions

Aqueous solutions of silver nitrate (SN) have found only some use. Lieser and Leckzyck[204] used an aqueous solution of SN to convert monobenzoyl methylxanthogenate α-methylglucoside into the corresponding thiolocarbonate. Thionocarbonate derivatives[205,206] were easily converted into carbonates using an SN solution in acetone, and thiopeptides[17,35] desulfurized into normal peptides in dioxan solution. The reaction of the monosodium form of 1,2:5,6-di-O-isopropylidene-D-mannitol with isothiocyanate did not form the expected phenylthiourethane derivative, but instead produced a cyclic carbonate together with its thionocarbonate or phenyliminocarbonate precursors depending upon the work-up conditions. The thionocarbonate was converted to the carbonate in 80% yield by reaction with silver carbonate in methanol.[207]

13.2.2. Gold(III) ions

Various gold(III) halogenides promote the hydrolysis of thioamides in aqueous solution in accordance with Scheme 51 to give the corresponding amides in high yields as the only organic products.[208-210]



$AuX_4^{\ominus}$ = $AuCl_4^{\ominus}$, $AuBr_4^{\ominus}$, $Au(CN)_2Br_2^{\ominus}$, $Au(NH_3)_2Cl_2^{\ominus}$

Scheme 51

Reactions involve the rapid and stoichiometric formation of the S-amide-gold(III) ion adduct, which

decomposes slowly to the O-amide. Comparison of results shows that, for square planar adducts, the rate of the desulfurization process is increased by an increase in (i) the positive charge on the gold atom and (ii) the softness of the attached ligands. In the presence of added ambient bromide ions the gold ions and adducts are partially or completely converted into octahedral species which undergo a more rapid desulfurization process. The halogen gold sulfide, which is presumably formed initially, undergoes further reactions and a brown precipitate containing gold and sulfur is eventually formed.

13.2.3. Iron(III) ions

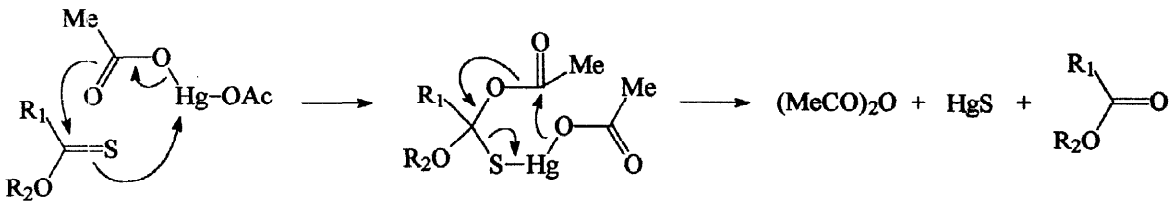
"Cayfen", i.e. clay-supported ferric nitrate, has been proposed by Laszlo *et al.*[211,212] as a simple and inexpensive reagent for the conversion of thioketones having aromatic substituents into the corresponding ketones. In most cases nearly quantitative conversions are achieved. It can also be applied to other thioketones such as fenchone (17%), dicyclopropyl ketone (39%), camphor (30%) or 2-adamantanone (68%), but yields are much smaller.

13.2.4. Copper(I) ions

Under a nitrogen atmosphere copper(I) chloride forms stable adducts with thiono-compounds, which when treated with sodium hydroxide as a 10% aqueous solution afford the corresponding carbonyl analogues.[213] Yields are greater than 85%. The method works well with a variety of thiono-compounds such as diphenylthiourea, thiobenzamide, thionicotinamide, 1-methyl-2-thiopyridone, thiocoumarine, 4,4'-dimethyl-thiobenzophenone, thioxanthione, Michler's thione and thiocamphor.

13.2.5. Mercury(II) ions

Ellis *et al.*[214] showed that the desulfurization of thioesters proceeds rapidly at room temperature using solutions of mercury(II) carboxylates (acetate, propionate, butyrate, valerate, pivalate, laurate) in chloroform, methylene chloride or pyridine. The rapid precipitation of mercuric sulfide by mercuric acetate in pyridine suggests the formation of a 1:1 complex which could rearrange *via* a cyclic transition state to give an ester as the principal organic product (Scheme 52).

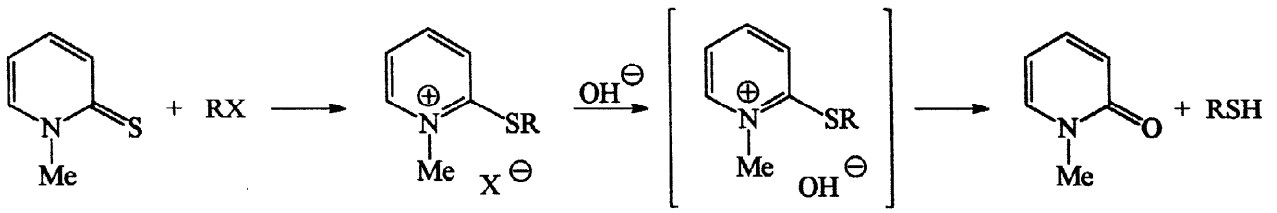


Scheme 52

The study of heterocyclic compound reactions showed that 1,2-dithiolo-3-thiones,[15,215-223] 1,3-dithiolo-2-thiones,[216,217,224] pyran-2-thiones,[225] thiopyran-2-thiones,[10] thiazoline-2-thiones,[226] thiazolidine-2-thiones,[227] 1,2,4-dithiazoline-3-thiones,[228,229] 1,4,2-dithiazole-5-thiones,[183] imidazoline-2-thiones,[230] pyrimidine derivatives[231-233] and 2-thioarylmethylene-2H-1,3,4-thiadiazolanes[234] were converted into the corresponding ketones by mercuric acetate in acetic acid. Thiopyran-2-thiones,[235] thiopyran-4-thiones[235-237] and benzo-3,1-thiazine-4-thiones[25] were converted by mercuric chloride. Cyclic and acyclic monothiocarbonates reacted with mercuric oxide to give carbonates.[186,238]

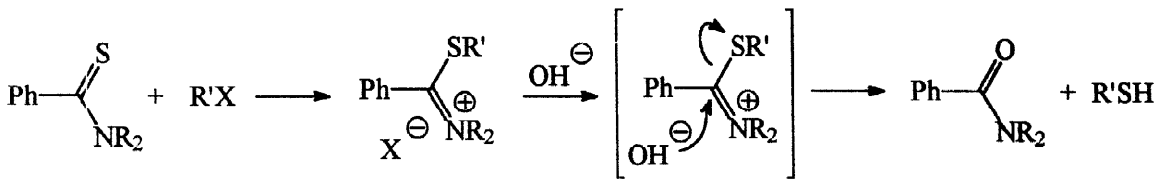
14. ALKYLATION FOLLOWED BY ALKALINE HYDROLYSIS

The alkylation of thioureas followed by basic hydrolysis is one of the methods for preparing thiols,[239] but it also affords carbonyl compounds corresponding to thioureas. N-Methyl-2(1H)-pyridone[240] was obtained from the corresponding pyridothione which was subjected to quaternization with primary and secondary halides, α-haloketones, α- and β-halocarboxylic esters and halosugar and then to alkaline hydrolysis (Scheme 53).



Scheme 53

N,N-Disubstituted thioamides, with or without benzylic α-protons on the thiocarbonyl carbon atoms, were converted to the corresponding amides in good yields upon treatment with trimethyl oxonium fluoroborate or methyl iodide under mild conditions.[241,242] Methyl sulfate can also be used an alkylating agent for thioamides which are then hydrolyzed in organic solvents containing small amounts of water to give amides[243] (Scheme 54).



Scheme 54

15. MISCELLANEA

15.1. N,N'-Sulfinyldiimidazole

Investigations of imidazole transfer reactions showed that N,N'-sulfinyldiimidazole[244] reacts with tertiary thioamides affording the corresponding amides in good yield, but the primary and secondary thioamides yield the corresponding nitriles and imidoylimidazoles, respectively.

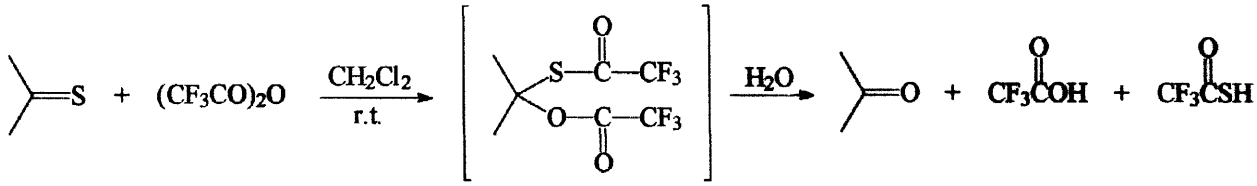
15.2. Trimethylphosphite, iron pentacarbonyl

Agosta and Ayral-Kaloustian[245] found a selective method for the conversion of thionoesters or thionolactones to the corresponding esters or lactones based on the use of dry, routinely-degassed trimethylphosphite or iron pentacarbonyl at 100°C for 340 and 3 hours, respectively. Mechanisms of these processes are not known.

15.3. Trifluoroacetic anhydride (TA)

TA[246] is a reagent which works very well with variety of thiocarbonyl heterocyclic compounds (thiolactams, thioketones and thiolactones). Use of this reagent has the advantage over other literature procedures of high yields, an easily handled reagent and a simple work-up process. Presumably, the reaction

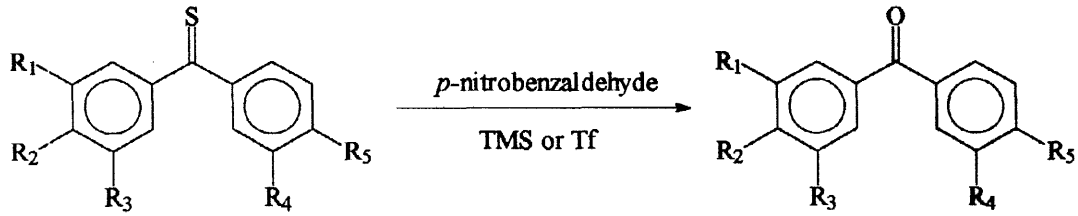
proceeds with formation of an adduct and subsequent very rapid hydrolysis on quenching with aqueous sodium carbonate to give the corresponding carbonyl compounds (Scheme 55).



Scheme 55

15.4. 4-Nitrobenzaldehyde and trimethylsilyl triflate (TMSOTf)

Ravindranathan *et al.*[247] described a simple and efficient procedure for the conversion of thiobenzophenone into benzophenone in high yield using 4-nitrobenzaldehyde in the presence of TMSOTf as the catalyst. However, thioamides and some aliphatic thioketones were found to be resistant under these conditions (Scheme 56).



Scheme 56

15.5. Halogen or pseudohalogen containing organic reagents

A variety of organic reagents containing halogen or pseudohalogen have also been used to convert thiocarbonyl compounds into carbonyl compounds. Among these are thiophosgene,[248,249] N-methylchloromethanimidoyl chloride,[248] thionyl[250,251] and oxallyl chloride,[250] N-bromosuccinimide,[252] cyanogen bromide[253] and iodosylbenzene[254] which convert some 1,2-dithiole-3-thiones,[248] thioamides,[249] thiopyran-[250] and pyran-4-thiones,[250] thioureas,[249,251,252] thiouridines[253] and 2-thiouracil and 4-thiouridine sites in tRNA[254] into the corresponding oxygen analogues through the initial formation of a salt or carbodiimide intermediate.

15.6. Iodocarbene

Singh and Singh,[255] during their investigations into the reaction of 4,4,6-trimethyl-1-phenyl-3,4-dihydropyrimidine-2(1H)-thione with iodocarbene, generated from iodoform and potassium *t*-butoxide, noticed the formation of a substantial amount of the pyrimidine-2(1H)-one.

15.7. Benzenesulfenyl chloride (BSCl)

Jørgensen *et al.*[256] showed that BSCl reacts with a series of thiocarbonyl compounds to give the corresponding carbonyl synthons in good yields.

15.8. Enzymes

Spector and Shideman[257] studied the metabolism of some thiopyrimidine derivatives such as thiamylal, thiopenatl and thiouracil, and found that thiamylal with minced rat liver resulted in the formation of a metabolite

which was isolated as secobarbital. Urine of rats which received thiouracil showed significant amounts of uracils.

16. CONCLUSIONS

It is apparent from the literature reviewed here that the many different methods through which a thiocarbonyl compound can be converted into a carbonyl compound, have had various degrees of success in relation to good yields and mild conditions used. Among these, hydrolytic methods catalyzed by metal ions are to be preferred, when they are possible, because they are cleaner than oxidative methods which give undesirable side products. Furthermore they have the advantage of simple isolation of the expected carbonyl compound because the sulfide can be separated with ease.

This review, although not exhaustive, attempts to help chemists who are carrying out >C=S → >C=O conversion in the choice of the most favourable method in relation to the type of thiocarbonyl compounds and the availability of reagents. Finally, our hope is that this review will help to stimulate renewed interest by synthetic and mechanistic chemists in this useful reaction.

AKNOWLEDGEMENTS

The authors are grateful to Italian M.U.R.S.T. for financial support.

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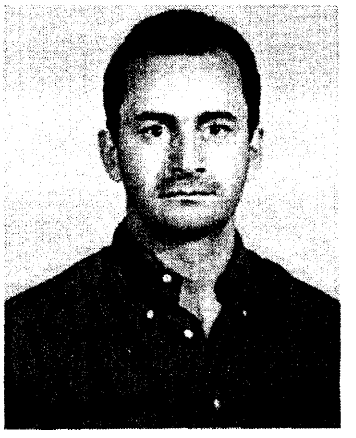

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