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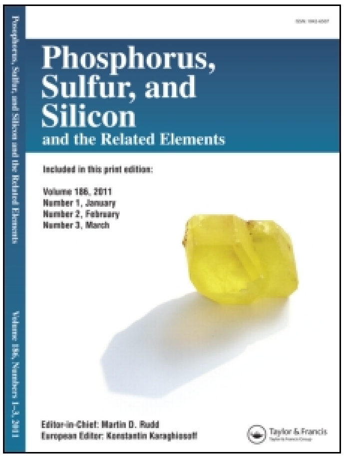

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Diacyl, Acyl Thioacyl, and DI(Thioacyl) Chalcogenides: Synthesis, Structure and Reactions

Shinzi Kato

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DIACYL, ACYL THIOACYL, AND DI(THIOACYL) CHALCOGENIDES: SYNTHESIS, STRUCTURE AND REACTIONS

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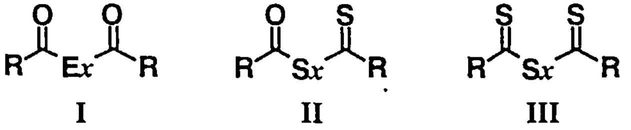
Abstract. The report covers the synthesis, spectra, structures and reactions of diacyl mono- and diselenides and tellurides, acyl thioacyl mono- and disulfides, and (dithioacyl) mono-, di-, tri- and tetrasulfides.

Introduction

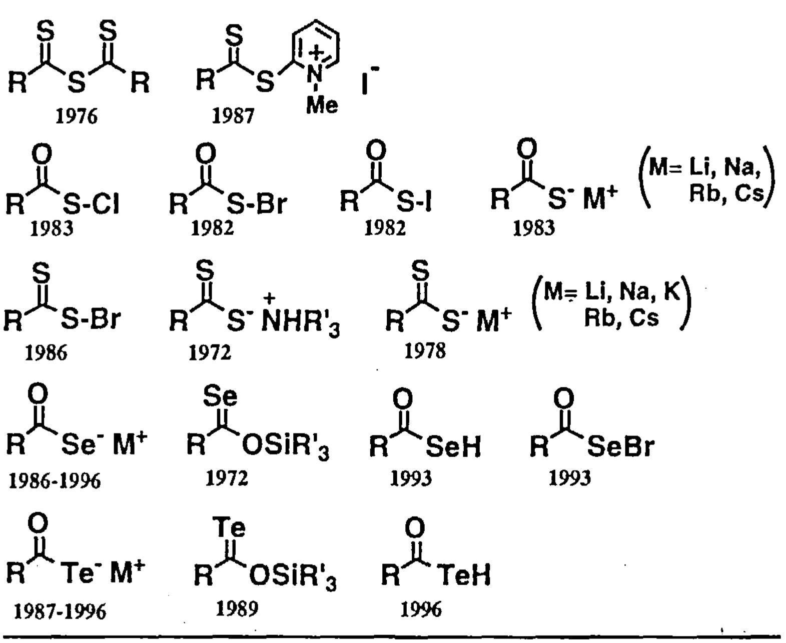
The chemistry of chalcogenocarboxylic acid derivatives has been extensively studied. Considerable attention has been paid to the synthesis and synthetic utility of thio- and dithiocarboxylic acid esters[1]. The purpose of this review is to describe our results regarding the chemistry of diacyl I, acyl thioacyl II, and di(thioacyl) chalcogenides III.



E= S, Se, Te. x= 1-4

There are generally considered to be 63 different chalcogenocarboxylic acid anhydrides, in which one to three oxygen atoms of the carboxylic acid anhydrides are replaced by sulfur, selenium or tellurium. In the case of diacyl peroxides with four oxygen atoms, the number of chalcogeno isologues increases to 275. However, except for symmetrical diacyl sulfides and disulfides and di(thioacyl) disulfides, a very few are known due to their instability and their difficult synthesis and purification[2]. We have

Table 1

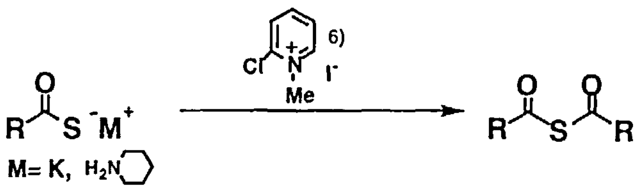


developed a variety of reactive reagents, including acylating, thioacylating and thio-, dithio-, seleno- and telluro-carboxylating reagents (Table 1). Using these reactive reagents, we have attempted to prepare various target compounds.

1. Synthesis

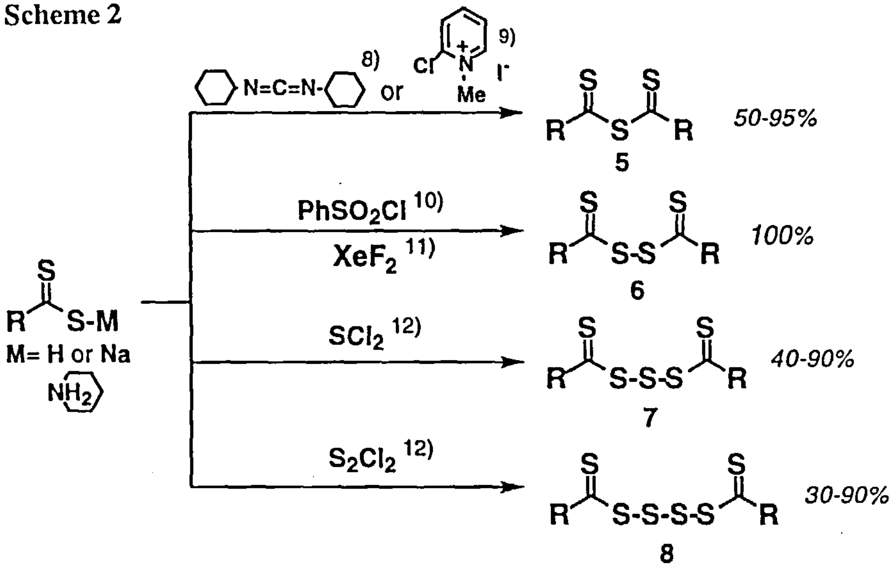
a) Diacyl sulfides. Methods for preparing diacyl mono- **1**$^{3)}$, di- **2**$^{4)}$, tri- **3**$^{5)}$ and tetrasulfides **4**$^{5)}$ have been developed by other groups. We have also developed an alternative and convenient method for preparing diacyl monosulfides **1** by reacting potassium thiocarboxylates with *N*-methyl-2-chloropyridinium salts $^{6)}$ (Scheme 1).

Scheme 1



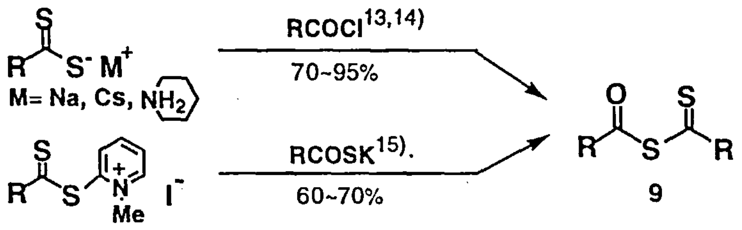
b) Dithioacyl sulfides. To our knowledge, only three aromatic di(thioacyl) disulfides have been described in the literature$^{7)}$. We have found that di(thioacyl) mono-, **5**$^{8\text{-}10)}$, di- **6**$^{11)}$, tri- **7**$^{12)}$ and tetrasulfides **8**$^{12)}$ can be readily prepared by the following reactions (Scheme 2)

Scheme 2

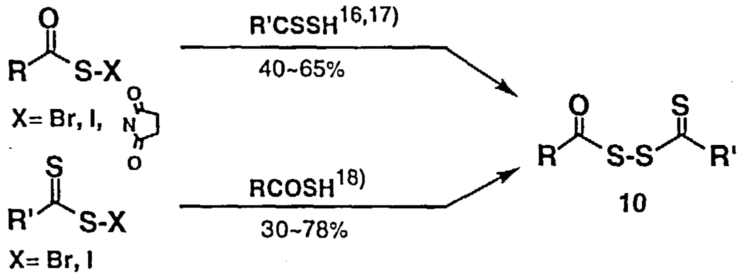


c) **Acyl thioacyl and di(thioacyl) sulfides.** In general, it is very difficult to prepare unsymmetrical sulfides which have acyl and thioacyl groups. In 1910, Houben reported the formation of acetyl thiobenzoyl sulfide7). We success-fully isolated acyl thioaroyl monosulfides 9 by reacting acyl chlorides with piperidinium or alkali metal dithiocarboxylates13-15) (Scheme 3).

Scheme 3



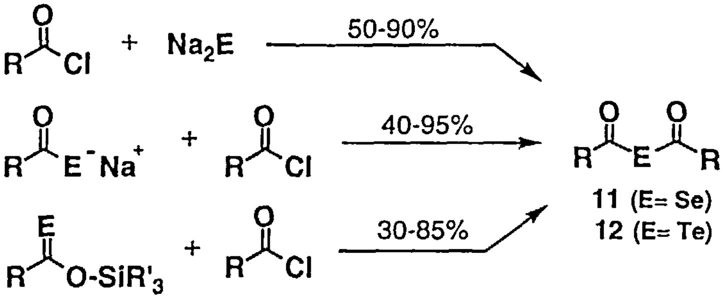
Scheme 4



In addition, we have found that *N*-acylthiosuccinimides[16] and acyl-[17,18] or thioacylsulfenyl halides[19] readily react with thio- or dithio-carboxylic acids to give unsymmetrical acyl thioacyl disulfides **10** in moderate to good yields (Scheme 4).

d) Diacyl selenides and tellurides. In 1968, Jensen, *et al.* reported the first preparation of diacyl selenide by the reaction of acyl chlorides with sodium hydrogen selenide[20]. On the other hand, the first diacyl telluride was reported in 1978 by Bergman and Engman, who synthesized tellurophthalic anhydride[21].

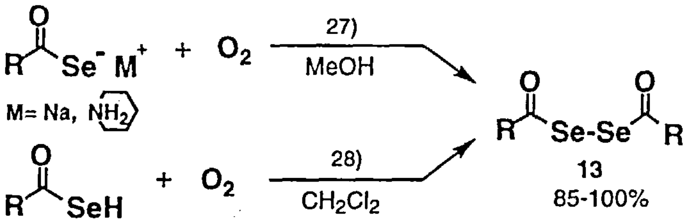
Scheme 5



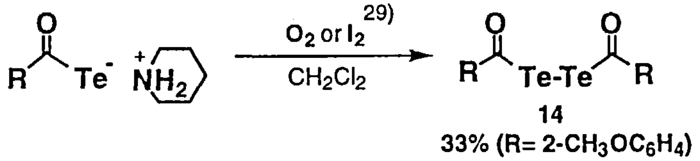
duMont, *et al.* isolated acyclic diacyl tellurides by reacting acyl chlorides with bis(trimethylsilyl) telluride[22]. We have also developed three methods for preparing diacyl selenides **11**[23,24] and tellurides **12**[25] (Scheme 5).

e) Diacyl diselenides and ditellurides. The preparation of diacyl diselenides was first reported in 1932 by Szepal and Wiorogorsky[26]. We have found that the oxidation of selenocarboxylic acid or its sodium salts with oxygen or iodine led to diacyl diselenide **13**[27,28] (Scheme 6). Although diacyl ditellurides **14** can be prepared by similar oxidation of alkali metal or *O*-trimethylsilyl tellurocarboxylates, the isolation is limited to the methoxy derivatives (14, R= 2-$CH_3OC_6H_4$)[29] (Scheme 7). Suzuki *et al.* also reported the preparation of the ortho methoxy derivative by reacting acyl chlorides with sodium hydrogen telluride[30].

Scheme 6

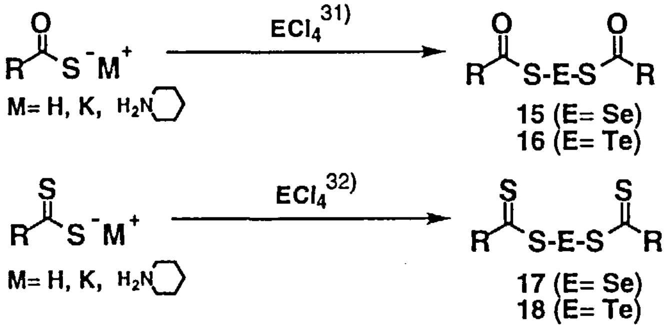


Scheme 7

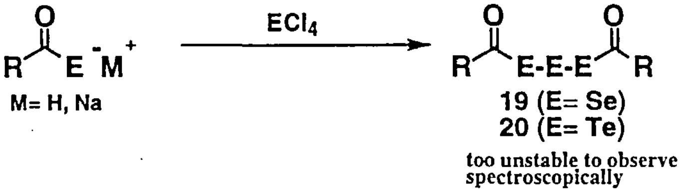


f) **Diacyl triselenides and tritellurides.** Since we had found that thio- and dithio-carboxylic acid piperidinium salts readily reacted with selenium and tellurium tetrahalides to give selenium and tellurium bis(thiocarboxylates) **15**, **16**$^{31)}$ and (dithiocarboxylates) **17**, **18**$^{32)}$ (Scheme 8), this reaction was applied to diacyl tri-selenides **19** and -tellurides **20**. However, several attempts to synthesize them under various conditions were unsuccessful most probably due to their extreme instability (Scheme 9).

Scheme 8

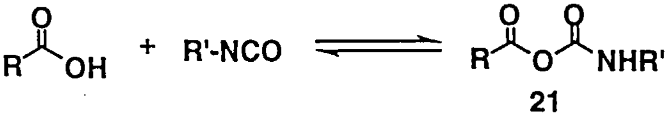


Scheme 9

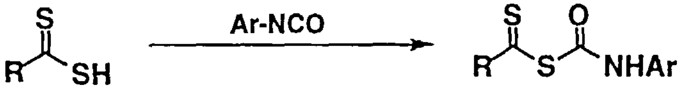


g) **Acyl carbamoyl chalcogenides.** In general, carboxylic acid carbamic acid mixed acid anhydrides **21** can not be isolated by reacting carboxylic acid with alkyl and aryl isocyanates due to equilibrium with the starting compounds (Scheme 10). In 1972, we found that thioacyl carbamoyl sulfides **22** were isolated from reaction of

Scheme 10

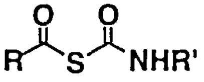


Scheme 11



22

dithiocarboxylic acids with aryl isocyanates (Scheme 11)[33]. Acyl carbamoyl 23 and thiocarbamoyl sulfides 24 have also been reported by other groups[34]. We recently succeeded in isolating crystalline seleno- 25[35] and tellurocarboxylic acid adducts 26[36].



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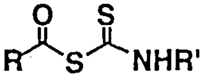

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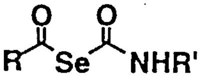

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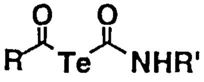

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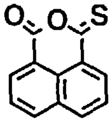
Acyclic acyl thioacyl and dithioacyl oxides can not be prepared due to extreme instability. However, the isolation of their cyclic derivatives such as 27 and 28 has been reported by Cava and his coworkers[37,38]. It should also noted that the spectroscopic observation of acyl selenoacyl oxides 29 was reported by Sonoda's group[39].



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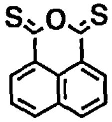

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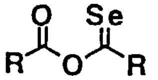
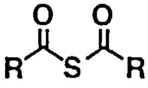
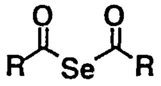
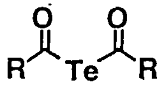
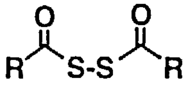
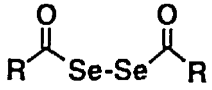
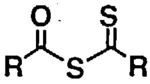
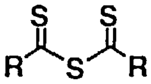
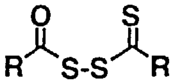
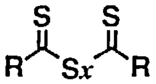


R= Ph, n-$C_{17}H_{35}$

29

2. Color and Spectra

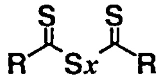
Table 2. The Color of Diacyl, Acyl Thioacyl and Di(thioacyl) Chalcogenides

 colorless	 pale yellow	 yellow	
 pale yellow	 yellow	 reddish orange to red	
 violet to sky blue	 purple to dark green	 red to reddish violet	 x= 2-4

The obtained diacyl chalcogenides are colorless to yellow. Diacyl ditellurides are reddish orange to red, although no absorption band is observed in the visible region. Acyl thioacyl disulfides and di(thioacyl) polysulfides are red to reddish violet. In contrast, acyl thioacyl monosulfides are violet to sky blue. Di(thioacyl) mono- sulfides are purple to dark green (Table 2).

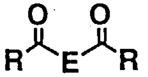
The n-π* transitions of di(4-methylbenzenethioyl) sulfides are shown in Table 3. The n-π* transitions of the monosulfide show a marked bathochromic shift compared to those of other polysulfides.

Table 3. The *n*–π* of Di(thioacyl) Sulfides

	λ max [nm] (CH_2Cl_2)			
R= 4-$CH_3C_6H_4$	*x* = 1	2	3	4
color	dark green	red	reddish violet	reddish pink
n–π*	584	522	530	527

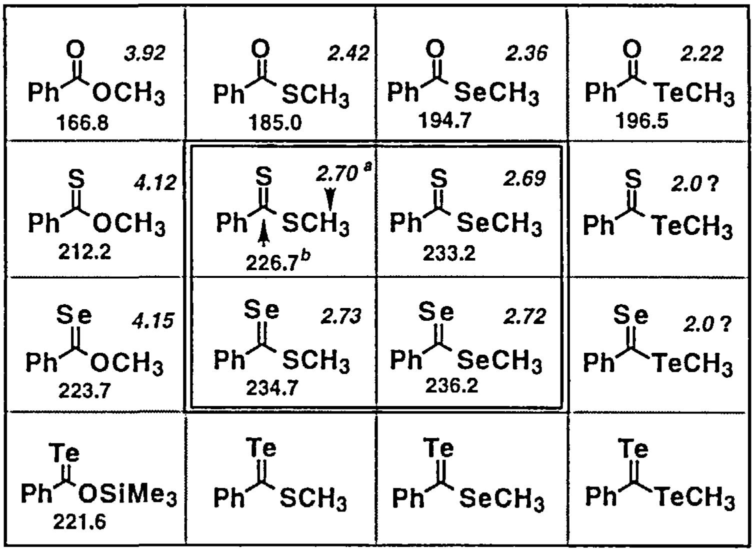
The carbonyl stretching frequencies and carbonyl carbon chemical shifts of diacyl chalcogenides are summarized in Table 4. The νC=O bands shift to a low frequency region in going from O to S, Se and Te. The carbonyl carbon signals show downfield shifts in the same order. Note that the values of the sulfur and selenium isologues are very close to those of the oxygen and tellurium isologues. This similarity in the spectral data between the sulfur and selenium isologues is also observed for other chalcogeno isologues. For example, in chalcogenoesters, the similarity of the methyl proton and thio- and seleno-carbonyl carbon chemical shifts is observed for the four isologues

Table 4. Spectral Data of Diacyl Chalcogenides

		IR (KBr)	^{13}C NMR (C_6D_6)
R	E	νC=O [cm^{-1}]	C=O [δ]
C_6H_5	O	1780, 1725	162.8
	S	1730, 1670	185.0
	Se	1722, 1670	188.4
	Te	1710, 1675	196.6

(dithio-, *S*-methyl selenothio-, *Se*-methyl selenothio- and diseleno-esters) in double square (Fig. 1).

Figure 1 ^{1}H and ^{13}C NMR of Chalcogenoesters

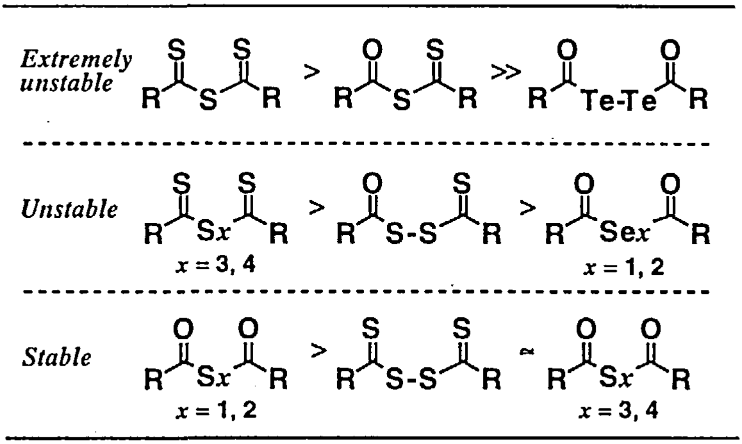


[a] ^{1}H NMR spectra (CH_3). [b] ^{13}C NMR spectra ($C=X$, X= O, S, Se, Te).

3. Stability

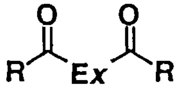
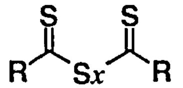
With regard to stability, the resulting chalcogenides can be roughly divided into 3 classes (Table 5). The top three compounds are extremely labile both thermally and towards oxygen. The middle three are considered unstable. In contrast, the bottom three are very stable.

Table 5. The Stability of the Chalcogeno Derivatives in Air



The stability of diacyl chalcogenides decreases in the order of oxygen, sulfur, selenium and tellurium (Table 6). Among di(thioacyl) sulfides, the disulfides are the most stable, while the monosulfides are the most labile both thermally and towards oxygen (Table 6).

Table 6. Stability in Air

	E
 x= 1 or 2	O > S > Se > Te
	x
	1 << 2 > 3 > 4 mono di tri tetra

4. Structures

Next, the structural aspect of some chalcogeno derivatives is discussed. Since we could not obtain single crystals of acyl thioacyl sulfides, the most stable conformations of acetyl thioacetyl[14)] and di(thioacetyl) sulfides[8b)] were calculated by the MINDO/3 method (Fig. 2). As shown in Figure 2, the diferences of both compounds exist at the thioacetyl moiety.

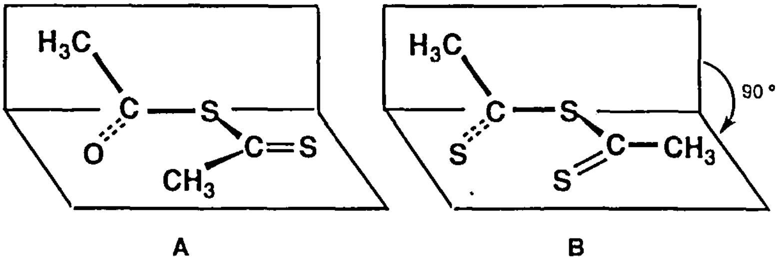


Figure 2. The most stable conformations of acetyl thioacetyl (**A**) and di(thioacetyl) sulfides (**B**) calculated by MINDO/3

Presumably, the overlap of the π-orbitals at the acyl thioacyl sulfide moiety is responsible to their color of the molecules.

In Figure 3, the X-ray structural analysis of di(2,4,6-trimethylbenzenethioyl) sulfides[40)] is shown. It is noted that the C=S lengthes of the two thiocarbonyl groups are different (1.616 and 1.603 Å). The distances (1.764, 1.755 Å) of the C-S single bonds also differ. The bond angle (113.2°) of C1-S1-C2 are normal.

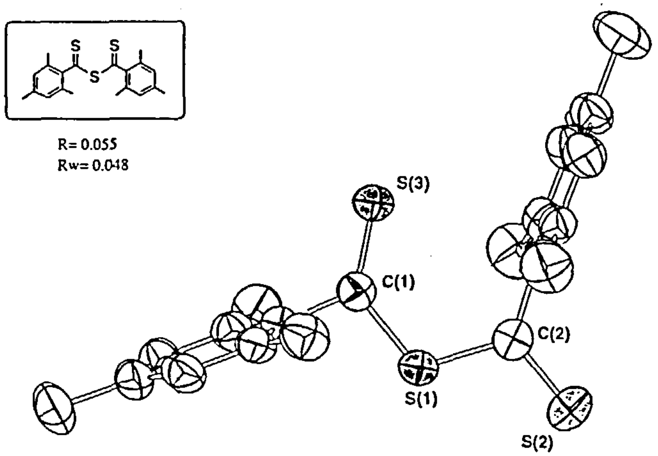


Figure 3. ORTEP Drawing of Di(2,4,6-trimethylbenzenethioyl) Sulfide

Figure 4 shows an ORTEP drawing of di-(2-methoxybenzoyl) disulfides41). The S-S bond length (2.039 Å) is longer than that (2.021 Å) previously reported for dibenzoyl disulfide (DBDS)42). The thiocarboxyl and 2-methoxy groups and the benzene ring are all in the same plane, which is almost perpendicular (94.2 °) to another plane in the molecule, while the corresponding angle in DBDS is 80. 8° (Fig. 5).

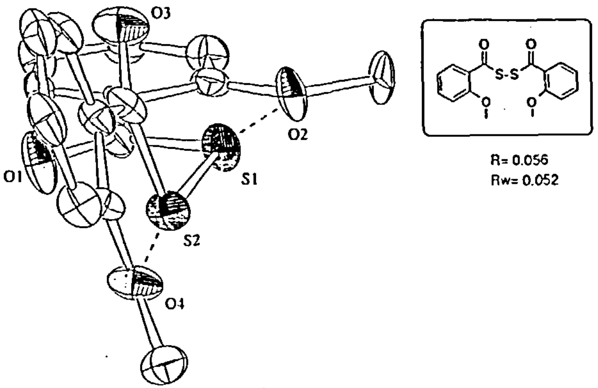
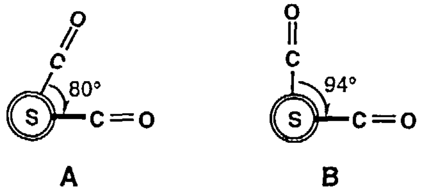


Figure 4. ORTEP Drawing of Di(2-Methoxybenzoyl) Disulfide



A B

Figure 5. The Dihedral Angles of Dibenzoyl Di-Sulfide (A) and Di(2-Methoxybenzoyl) Disulfide (B)

O2-S1 and O4-S2 distances are 2.65 and 2.67 Å, which are shoter (ca. 0.6 Å) than the van der Waals radii (3.25 Å) of the oxygen and sulfur atoms. O2-S1-S2-O4 is almost linear. These results indicate an intramolecular interaction between the antibonding orbitals of the sulfur-sulfur bond and the nonbonding orbitals of the methoxy oxygen.

Figure 6 shows an example of diacyl diselenide[43]. In this case, the intramolecular interaction between the methoxy oxygen and the selenium is one-to-one (the distance between selenium and the methoxy oxygen is very short; 2.65 Å). The opposite methoxy oxygen is free. As mentioned above, the isolation of diacyl ditellurides was possible only for 2-methoxy derivative due to their extreme instability[29]. This is resumably that the ditelluride is stabilized by similar intramolecular interaction between the ortho methoxy oxygen and the tellurium atoms (Figure 7).

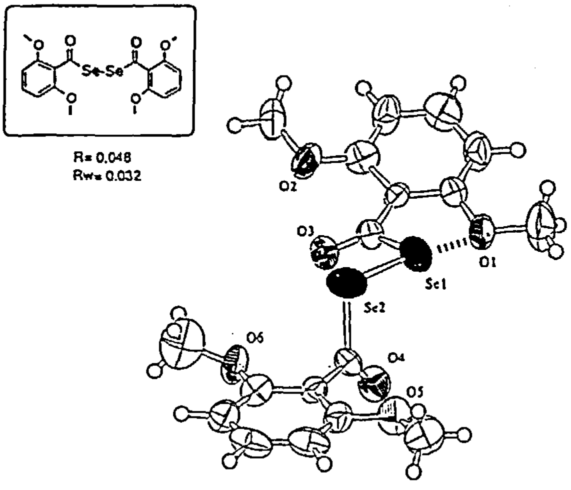


Figure 6. ORTEP Drawing of Di (2,6-dimethoxybenzoyl) Diselenide

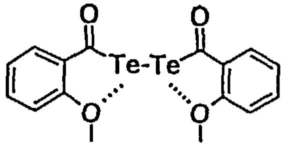


Figure 7. Di(2-methoxybenzoyl) Ditelluride

Previously, we isolated various crystalline thioacyl carbamoyl sulfides 22 and proposed on the basis of their IR spectral data that they have a six-membered ring structure due to intramolecular hydrogen-bonding between thiocarbonyl sulfur and the NH hydrogen atoms, which enhances their stability[32]. This was supported by X-ray structural analysis. Figure 8 shows an ORTEP drawing of 4-methoxybenzenethioyl 4-methylbenzenecarbamoyl sulfides. The molecule is planar, and six-membered ring structure is hydrogen-bonded between the thiocarbonyl sulfur and the NH hydrogen atoms[44].

atoms[44].

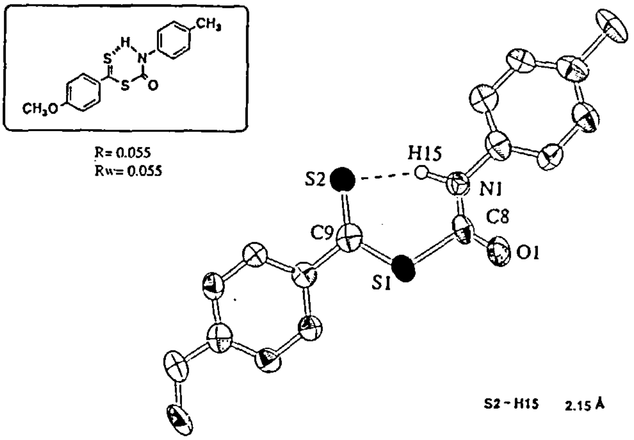


Figure 8. ORTEP Drawing of 4-Methoxybenzenethioyl 4-Methylbenezenecarbamoyl Sulfude

The structure of the thiocarboxylic acid adduct was also revealed by X-ray stractural analysis, in which involved a six membered structure due to the hydrogen bonding between the carbonyl oxygen and the NH hydrogen atoms [44] (Fig. 9).

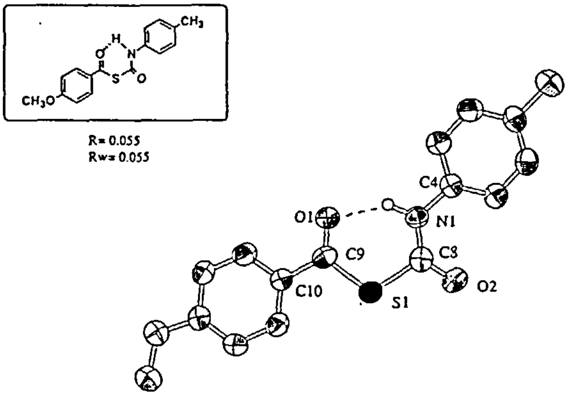
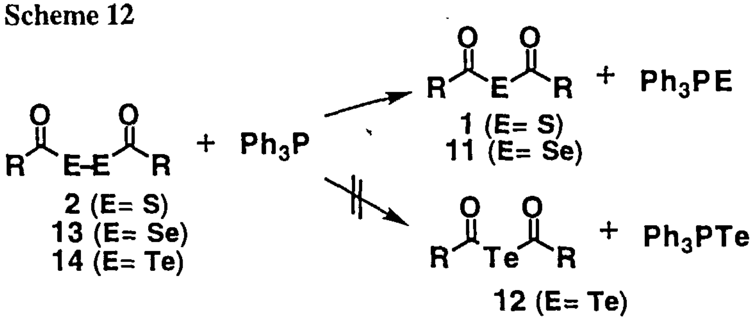


Figure 9. ORTEP Drawing of 4-Methoxybenzoyl 4-Methylbenzenecarbamoyl Sulfide

5. Reactions

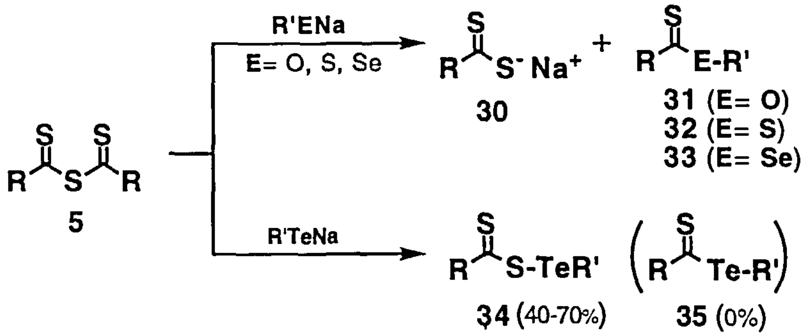
It is noted that diacyl ditelluriders are not detellurized by triphenylphosphine below 0 °C, although diacyl disulfides and selenides readily react with triphenylphosphine to afford the corresponding diacyl sulfides and selenides in almost quantitative yields, respectively[45] (Scheme 12).

Scheme 12



It is well known that diacyl sulfides react with sodium alcoholates to afford the corresponding esters and sodium thiocarboxylates. We examined the reactions of dithioacyl sulfides with sodium alcoholates and thio-, seleno-, and tellurolates[45]. The reactions with sodium alcoholates and thio- and selenolates were found to afford both of the corresponding dithiocarboxylic acid sodium salts **30** and esters **31-33**. In contrast, the reaction with sodium tellurolate led only to phenyltellurenyl dithiocarboxylates **34**, instead of tellurothioesters **35** (Scheme 13).

Scheme 13



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