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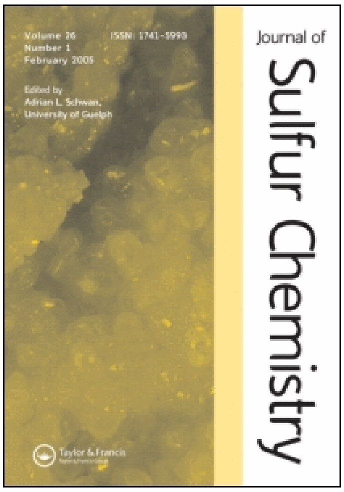

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The Chemistry of Carbon Subsulfide

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THE CHEMISTRY OF CARBON SUBSULFIDE

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This review summarizes the syntheses and reactions of carbon subsulfide, S=C=C=C=S. Carbon subsulfide can be synthesized for preparative purposes by decomposition of carbon disulfide in an electric arc. For spectroscopic purposes the thermolysis of S-heterocyclic precursors is described as a way which has found much interest. Reactions of carbon subsulfide are mainly cyclizations with 1,3-binucleophilic agents to give six-membered heterocycles, oxidative addition of platinum metal complexes or self-condensation to polymeric $(C_3S_2)_x$.

Keywords: Carbon subsulfide; cyclization; polymerization; 1,2-propadiene-1,3-dithione; thiopyronethiones

CONTENTS

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1. BACKGROUND ON CARBON SUBSULFIDE

Heterocumulenes have attracted great theoretical and astrophysical interest in recent years. Among them carbon subsulfide C_3S_2 is one of the few members of this class which is stable enough to allow handling at room temperature for a short time. Because of its stability it has been used to a certain extent in synthetic inorganic and organic chemistry.

In 1893, the Hungarian chemist von Lengyel[1] discovered that the action of an electric arc on the vapor of carbon disulfide formed a red, lachrymatory liquid, which he called *tricarbonium disulfide* according to its elemental analysis. This compound was found to polymerize easily, especially with acids or bases as catalysts. The preparation method developed by von Lengyel[1] is still used with some modifications. In 1912, Stock and Praetorius[2] investigated this compound thoroughly, improved its preparation, elucidated the structure by reaction to the already known dithiomalonodianilide, and assigned to this compound the name *carbon subsulfide* because to its analogy to carbon suboxide.

Carbon subsulfide is named systematically according to the IUPAC rules as 1,2-propadiene-1,3-dithione, but its trivial name is usually used. In several reviews different aspects of carbon subsulfide chemistry are treated. The earlier results on carbon subsulfide are reported in *Chemical Reviews*,[3] aspects of organic synthesis are found in *Houben-Weyl*[4,5] and in *Chemiker-Zeitung*,[6] and inorganic and physical aspects can be found in *Gmelin*[7] and in *Polyhedron*.[8]

2. PHYSICAL PROPERTIES AND STRUCTURE OF CARBON SUBSULFIDE

Since 1965 the structure elucidation of carbon subsulfide especially by spectroscopic methods has found increasing interest. Many investigations have been performed and interatomic distances and angles have been determined. Much work has been done in order to solve the question if the S=C=C=C=S molecule possesses a linear or a bent structure. The spectral investigations include infrared spectra,[9–17] Raman spectra,[10,13,18,19] UV/vis spectra,[20–22] photoelectron spectra[22] and phosphorescence spectra.[23] Structural calculations based on spectral data can be found in Refs. [10–12,14,15,19,22,24–32], physical data of carbon subsulfide can be found in Refs. [33–37]. A short summary about physical and spectral properties of carbon subsulfide can be found in *Gmelin*.[7] Detailed reviews about spectrometric[38] and theoretical studies[39] on carbon subsulfide can be found in this journal.

The boiling point of carbon subsulfide is 60–70 °C at 12 Torr and the melting point −0.5 °C (the online database *Beilstein Crossfire* reports the wrong information that in one of our papers on carbon subsulfide[40] a mp of 135 °C should be given). The density $D_{15} = 1.319\,\mathrm{g\,cm^{-3}}$.

3. PREPARATION OF CARBON SUBSULFIDE

The greatest problems with the synthetic chemistry of carbon subsulfide are – besides its instability – the low yields and the impurities which the known synthesis methods suffer from. For synthetic purposes, only the reaction of carbon disulfide in an electric arc has been used, all other methods failed to give preparatively useful results.

3.1. By Arc Discharge

The decomposition of carbon disulfide in an electric arc (see Scheme 1) is the oldest method but it has been used so far in most cases for the preparation of carbon subsulfide. The action of the discharge on carbon disulfide is interpreted both as a thermal decomposition reaction[2] and as a reduction of the carbon disulfide by the action of the electric current,[42] because only the use of DC voltage gives carbon subsulfide, whereas AC prevents the formation of carbon subsulfide.

$$3\,CS_2 \xrightarrow[-4\,S]{\text{arc discharge}} S{=}C{=}C{=}C{=}S$$

SCHEME 1 Decomposition of carbon disulfide in an electric arc.

3.1.1. In Gaseous Carbon Disulfide

The general principle of this method has already been described in detail by von Lengyel,[1] using an electric arc between two graphite electrodes in the vapor of carbon disulfide vapor. Most of the scientists working on carbon subsulfide[2,6,9,15,21–23,33,42–45] have used this method with some modifications.

We used for this synthesis method[6] an apparatus assembled from commercially available glassware for most of its parts (see Figure 1). A modified 2000 mL *Quickfit* reaction flask with a plane joint was used as reactor. This flask was modified as a double wall reactor for water cooling and at the bottom a ground glass joint allows to connect a 500 mL round bottomed flask which contains the carbon disulfide to be evaporated. The plane joint lid is equipped with five ground glass joints which allow all necessary functions to be performed from the top. The central joint contains the stirrer guide and a modified agitator shaft of a mechanical stirrer. The connection of the vertical movable graphite cathode (12 mm diameter) runs through the agitator shaft, thus making it possible to adjust the distance between the electrodes. The fixed graphite anode (14 mm diameter) is connected through one of the other ground glass joints. The power supply consists of brass rods which are glued to the joints gasproof and solvent resisting. The other three ground glass joints allow the connection of a jacketed coil reflux condenser, a connection for protective gas (nitrogen) and of a sensor for temperature control. The gas outlet runs through the condenser fitted with a bubbler.

For safety purposes a protective screen is placed in front of the apparatus, and the adjustment of the electrodes during the reaction is made possible by a shaft which is long enough to be handled from the side. The power supply generates 36 V DC voltage. As overload protection a resistor with a high power rating (2 Ω, about 200 W) is used.

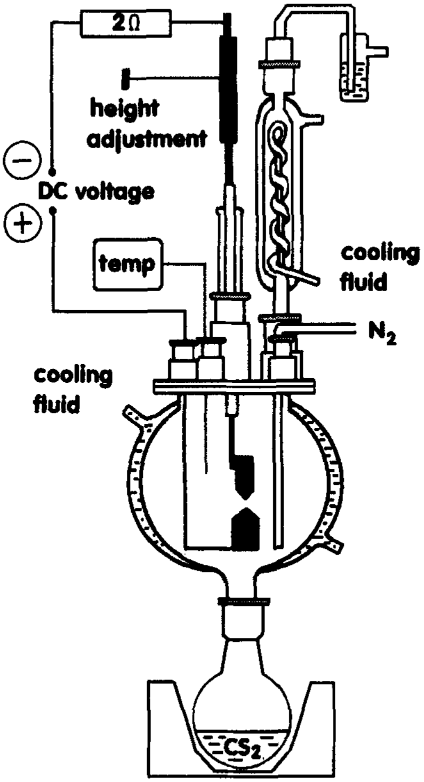


FIGURE 1 Experimental setup for the vapor-phase pyrolysis of carbon disulfide in an arc discharge.

To start the preparation, the 2000 mL reactor is cooled with water, and in the whole system the air is replaced by nitrogen in order to avoid explosions. Then carbon disulfide (150–200 mL) in the 500 mL round bottomed flask is heated to boiling and the arc discharge started by a short circuit between the electrodes. Under running conditions the electrode tips are only separated by a few millimeters and the voltage across the electrodes drops to about 25 V while a current of about 7 A is maintained. When the temperature of the vapor phase is above 60 °C, the reactor is allowed to cool some minutes in order to avoid polymerization. After a few hours the carbon disulfide solution turns orange-brown, and after 4–6 h the pyrolysis is stopped, black polymer products are filtered off and excess carbon disulfide is removed by distillation *in vacuo*.

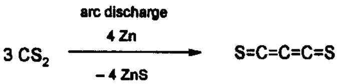
Further purification and isolation is not necessary for preparative purposes, because the concentrated solution of carbon subsulfide is allowed to react quickly with the corresponding substrates. The yield is estimated to be about 100 mg, determined by reaction with bromine (see Section 4.2).

Holland *et al.*[15] have reported a method very similar to ours, however with a higher voltage (100 V) and stronger current (23 A). Their isolation of carbon subsulfide is performed by trap to trap distillation; they obtain pure carbon subsulfide, a bright red liquid, mp 0 °C, which is stored at liquid nitrogen temperature. The authors do not give a yield, but state that they obtained only small yields of relatively pure carbon subsulfide which was used for spectroscopic purposes.

For spectroscopic purposes only a modified vapor phase pyrolysis in an electric arc has been reported. Takeuchi and Tasumi[23] prepared carbon subsulfide by passing a gas mixture of carbon disulfide and argon through a pyrex tube in which an electric arc is produced by a Tesla coil. Brown products are deposited gradually inside the pyrex tube, gaseous products together with unreacted carbon disulfide are introduced to a vacuum chamber and then immediately condensed on a silver-coated copper block cooled to 20 K by a helium refrigerator. The discharge products were identified by their infrared spectra upon condensation on a caesium iodide plate.

3.1.2. *In Liquid Carbon Disulfide*

Stock and coworkers[2,41] developed another arc discharge method for this preparation which was running in liquid carbon disulfide using an antimony/graphite or a zinc electrode as anode material. With this method, yields of about 1.25 g have been reported, which should make this method best suitable for preparative purposes. This method has been used by some scientists[6,10,20,40,45] for the preparation of carbon subsulfide, but less frequently than the vapor phase pyrolysis.



$$3\,CS_2 \xrightarrow[-4\,ZnS]{\text{arc discharge}\atop 4\,Zn} S{=}C{=}C{=}C{=}S$$

SCHEME 2 Decomposition of carbon disulfide in an electric arc with a zinc electrode.

We used for this method most parts of the apparatus described in Section 3.1.1, except the reactor, which was replaced with a commercially available 2000 mL *Quickfit* reaction flask with a plane joint (see Figure 2). The upper part of the apparatus was used as described above. As electrodes a vertical movable graphite cathode (12 mm diameter) and a fixed zinc anode (6 mm diameter) were applied. The 2000 mL flask is filled with 1500 mL carbon disulfide and the air replaced by nitrogen in order to avoid explosions. During this time the flask is cooled in a bath filled with ethanol which is held at −25 °C.

The arc discharge is started by a short circuit between the electrodes. Under the operating conditions the electrode tips are only separated by a few millimeters and the voltage across the electrodes drops to about 25 V while a current of about 7 A is maintained. This equipment allows

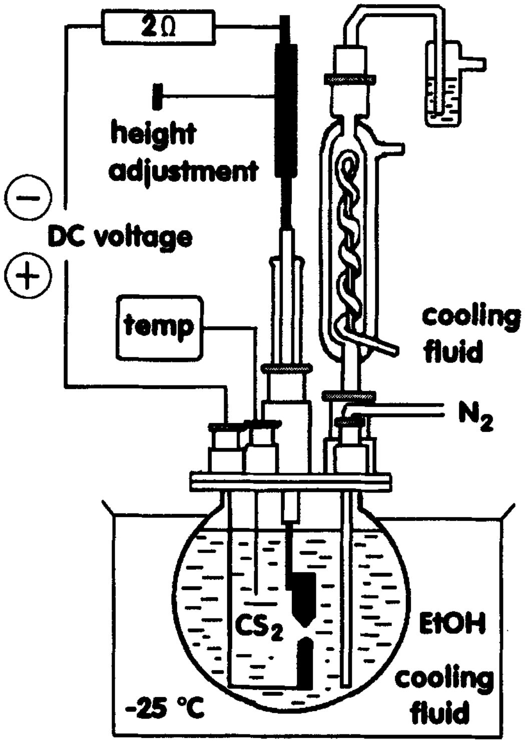


FIGURE 2 Experimental setup for the pyrolysis of liquid carbon disulfide by an arc discharge.

a reaction time of about 10 min at 0 °C, then the discharge has to be stopped to cool down the system. The liquid is soon colored black by zinc sulfide which forms during the pyrolysis. After a running time of the arc discharge of about 3 h, which corresponds to a working life of about 6–8 h, the liquid is filtered off from black solid material and the excess carbon disulfide removed by distillation *in vacuo*; the zinc consumption is about 3–4 g, nearly double the amount reported in Ref. [41]. The yields of carbon subsulfide, however, which were determined by reaction with bromine (see Section 4.2), were lower than with the vapor phase method, and less than a tenth of the yield reported by Stock *et al.*[41]

3.2. *By Thermolysis*

Besides the pyrolysis of carbon disulfide in an electric arc, some attempts have been made to obtain carbon subsulfide by pyrolysis without the action of an electric discharge.

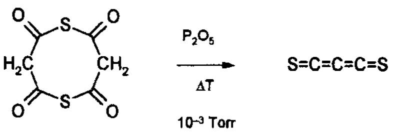
3.2.1. *Of Carbon Disulfide*

The pyrolysis of carbon disulfide in a quartz tube above 900 °C has been reported by Stock and Praetorius[2] and by Arctawski[46] to give carbon subsulfide in low yields with many polymerization by-products. Similar results have been reported by Budnikov and Bobrovnik[47] concerning the catalytic pyrolysis of carbon disulfide and by Wibaut[48] concerning the pyrolysis of sulfur-containing coal. None of these methods, however, gives carbon subsulfide on a preparatively useful scale and purity. Flash vacuum pyrolysis of carbon disulfide[51] does not yield carbon subsulfide.

3.2.2. *Of S-heterocyclic Precursors*

The first attempt to obtain carbon subsulfide from a heterocyclic precursor molecule was the pyrolysis of dimeric malonothioanhydride in the presence of phosphoruspentoxide by Diels *et al.*,[49] which gave only traces of carbon subsulfide.

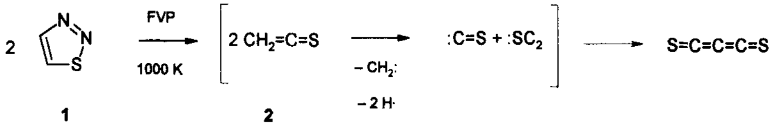
However, in the last decade of the 20th century, this general synthetic route has attracted exceptional interest, and a number of molecules



SCHEME 3 Vaccum pyrolysis of dimeric malonothioanhydride.

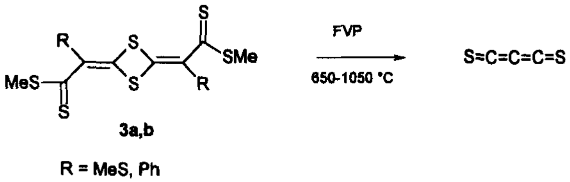
have been found to give carbon subsulfide by flash vacuum pyrolysis (FVP).

Holland *et al.*[15] have reported a method which involves the flash vacuum thermolysis of 1,2,3-thiadiazole **1** (see Scheme 4), prepared by the method of Hurd and Mori.[50] When it was passed through a quartz tube at temperatures above 1000 K, carbon subsulfide was generated, which was collected at an infrared absorption cell. The yield of this method is reported to be better than that of the arc discharge route in carbon disulfide vapor, but the purity is lower because of the formation of many by-products. The mechanism is assumed to start with the formation of thioketene **2** from **1**. The additional by-products are assumed to stem from secondary decomposition of thioketene **2** and not from the precursor **1**. The reaction time scale and the absence of hydrogen sulfide among the products point to a specific free radical mechanism.



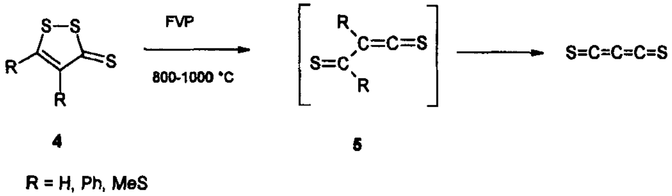
SCHEME 4 Flash vacuum pyrolysis of 1,2,3-thiadiazole.

Kappe *et al.*[51] observed the formation of carbon subsulfide in the FVP of the 1,3-dithiethanes **3a** and **3b** (see Scheme 5). On a preparative scale, **3b** was sublimed at 200 °C through a hot quartz tube at 650–1050 °C over 3 h, the pyrolysis products were collected on a liquid nitrogen cool finger and the compounds washed off the finger with chloroform. For matrix isolation of pyrolysis products of **3a** and **3b**, samples were codeposited with argon on barium fluoride disks and infrared spectra recorded to identify carbon subsulfide. The formation of carbon subsulfide from **3a** has also been observed by mass spectrometry.[53]



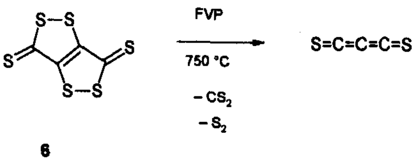
SCHEME 5 Flash vacuum pyrolysis of 1,3-dithiethanes.

Pedersen *et al.*[51,52,54,55] have shown that carbon subsulfide is formed in substantial amounts by FVP of 1,2-dithiole-3-thiones **4** (see Scheme 6). The thioacylketenes **5** are assumed to be the intermediates. The FVP apparatus employed a quartz tube (100 × 80 mm) and a liquid helium cryostat for argon matrix isolation. The pressure was about 10^{-6} mbar, the pyrolysis temperature 800–1000 °C. The amount of carbon subsulfide was determined by comparison of the carbon subsulfide peak with the carbon disulfide peak. Hitherto, however, no preparative method on this basis has been published.



SCHEME 6 Flash vacuum pyrolysis of 1,2-dithiole-3-thiones.

Another molecule, which was found by Pedersen *et al.*[56] to give carbon subsulfide on pyrolysis, is 1,2-dithiolo[4,3-*c*]1,2-dithiole-3,6-dione **6** (see Scheme 7).



SCHEME 7 Flash vacuum pyrolysis of 1,2-dithiolo[4,3-*c*]1,2-dithiole-3,6-dione.

So far, all these methods suffer from three disadvantages: (1) the preparation of the starting materials on a large scale is rather tedious, and, more important, (2) hitherto, no preparative method on the basis of the reactions described in Schemes 4–7 has been established; (3) all these methods give carbon subsulfide of a rather low purity.

3.3. By Photolysis

Nicholes *et al.*[57] have reported a simple method, which should give carbon subsulfide in low yield by photolysis of carbon disulfide with UV light of 290–360 nm generated with a mercury vapor lamp. We have repeated this reaction, and irradiated carbon disulfide for 5 h under ice cooling with a mercury vapor lamp giving 360 nm UV light.[6] However, we could not isolate or detect (by trapping with aniline) any traces of carbon subsulfide; the only product was the $(C_3S_2)_x$ polymer (see Section 4.7). Strauss and Steudel[58] described similar unsuccessful results when they photolyzed sulfur in carbon disulfide, and Cataldo[59] reported the formation of the $(C_3S_2)_x$ polymer by photopolymerization of carbon disulfide.

3.4. By Other Methods

Steudel[60,61] found that carbon disulfide decomposed in a high frequency electric field to give, in very low yield, carbon subsulfide. Another method, which was reported by Quellhorst and Binnewies,[62] uses the treatment of pure carbon disulfide with ultrasound at a frequency of 20 kHz. Small amounts of carbon subsulfide were obtained, but also this method is not suitable for a preparative synthesis of carbon subsulfide.

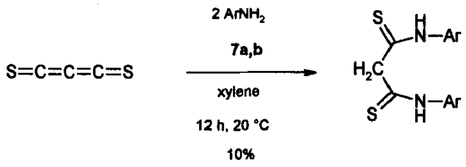
4. REACTIONS OF CARBON SUBSULFIDE

Although carbon subsulfide is one of the few heterocumulenes which are stable enough for synthetic purposes, only a few reactions have been described which lead to well-characterized compounds, in contrast to the oxo analogue carbon suboxide, which has found broad application in organic synthesis.[63] The reasons which explain this lack of organic reactions are on one hand the difficulties encountered in the tedious preparation of carbon subsulfide with its low yields, and on the other hand its instability, which does not allow a longer storage and forces one to perform all reactions immediately after the synthesis. A third point is that carbon subsulfide is rather unreactive which often gives unwanted side products.

4.1. Formation of Malonamides

Carbon subsulfide can be regarded as intramolecular anhydride of malonic acid. The reaction of carbon subsulfide with the arylamines **7a,b** gives the corresponding dithiomalonodiamides **8a,b** (see Scheme 8). The formation of **8** is related to the similar reaction of aniline with carbon suboxide[63] and was used by Stock and coworkers as proof for the constitution of carbon subsulfide.[2,41,42] They synthesized dithiomalonodianilide **8a** and dithiomalono-bis(2-naphthylamide) **8b**.

We also applied this reaction for a rapid detection of carbon subsulfide[6,40] by thin layer chromatography. For the preparation of **8a**[40] we used unpurified carbon subsulfide (50 mg), which was synthesized by arc discharge of carbon disulfide (see Section 3.1.1), filtered and taken to dryness *in vacuo*; reaction with aniline (1.0 g) for 12 h at room temperature followed by chromatographic separation on a silica gel column gave 15 mg of the anilide **8a**. The reaction of aniline with a carbon subsulfide solution in carbon disulfide, obtained by the arc discharge pyrolysis followed by filtration, gave only a small yield of **8a** besides a large amount of *N*,*N'*-diphenylthiourea. Elemental analysis, mass spectral data and comparison with dithiomalonodianilide prepared according to Ref. [64] confirmed the structure of **8a**.



8a, b

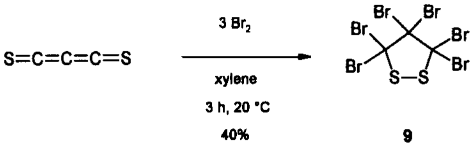
a: Ar = Ph **b**: Ar = 2-naphthyl

SCHEME 8 Reaction of carbon subsulfide with arylamines.

4.2. Addition of Bromine

The reaction of carbon subsulfide with bromine (see Scheme 9) has been known since the discovery of carbon subsulfide by von Lengyel[1] and was also used by Stock *et al.*[2,41,42] A hexabromide, $C_3S_2{\cdot}6Br_2$, is obtained, which can be used for the rapid determination of the yield of carbon subsulfide. On the basis of this reaction[40] we determined our yields using the arc discharge routes (3.1.1 and 3.1.2) and found typical yields of 90 and 50 mg respectively for these synthetic routes.

The formation of a hexabromide is a typical reaction of carbon subsulfide. In contrast to this, carbon suboxide gives with bromine a tetrabromide, namely dibromomalonyl dibromide.[63] The infrared spectrum, mass spectrum and elemental analysis indicate the structure of 3,3,4,4,5,5-hexabromo-1,2-dithiolane,[40] a reaction which involves both the addition of bromine to the heterocumulene and oxidation by bromine to the disulfide **9**.



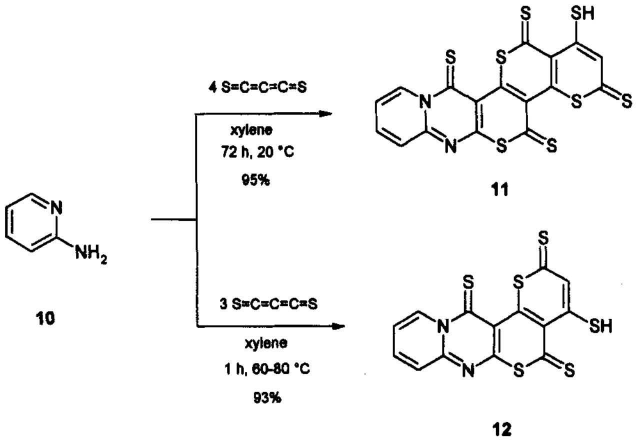
SCHEME 9 Reaction of carbon subsulfide with bromine.

4.3. *Formation of Six-membered Heterocycles*

Ring closure reactions of carbon suboxide with 1,3-binucleophiles are well known[63] and give six-membered heterocyclic compounds depending on the structure of the binucleophile. These results prompted us to transfer these findings to carbon subsulfide.

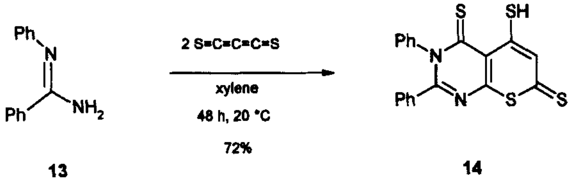
2-Aminopyridine **10**, having a 1,3-binucleophilic amidine structure $NH_2{-}CR{=}NR$, is known to react with carbon suboxide at room temperature to give a undefined mixture of compounds; only at −70 °C the monofused 4*H*-pyrido[1,2-*a*]pyrimidine-2,4-dione was obtained.[63] With carbon subsulfide, 2-aminopyridine **10** reacted at 20 °C very slowly to give in low yields a tetra-adduct, 1-mercapto-4,6,14-trithia-7,12-diazabenzo[*b*]chrysene-3,5,13,15-tetrathione (**11**)[45,65] (see Scheme 10). Raising the temperature to 60–80 °C gave after 1 h reaction time a tris-adduct, 4-mercapto-1,6-dithia-7,12-diazabenzo[*a*]anthracene-2,5,13-trithione (**12**).[45]

N-Phenylbenzamidine **13**, having again the 1,3-binucleophilic amidine structure $NH_2{-}CR{=}NR$, reacts slowly with carbon subsulfide at



SCHEME 10 Reaction of carbon subsulfide with 2-aminopyridine.

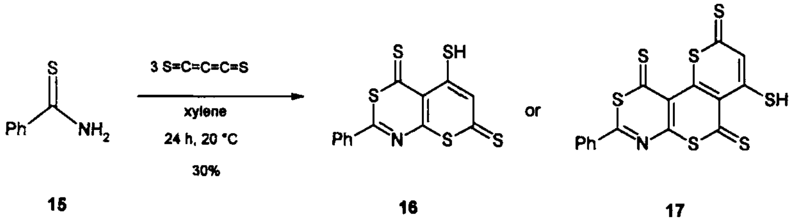
ambient temperature to give the 1 : 2 adduct, 5-mercapto-2,3-diphenylthiopyrano[2,3-*d*]pyrimidine-4,7(3*H*)-dithione (**14**)[45] (see Scheme 11).



SCHEME 11 Reaction of carbon subsulfide with N-phenylbenzamidine.

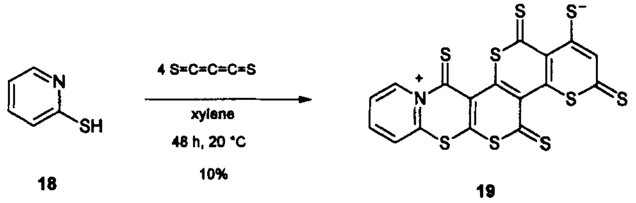
The mass spectra[45] of **11**, **12**, and **14** show only the masses of the monoadducts, whereas the elemental analyses correspond exactly and reproducibly to the corresponding oligoadducts. The infrared spectra[45] are similar to the spectra obtained from polymeric carbon subsulfide.[43] *N*-Substituted 2-aminopyridines and *N*,*N*′-disubstituted benzamidines, which were found to react with carbon suboxide to give cross-conjugated six-membered betaines,[63] fail to react with carbon subsulfide.[45]

Thiobenzamide **15**, having the 1,3-binucleophilic thioamide structure $NH_2{-}CR{=}S$, reacts rapidly with carbon subsulfide to give a good yield of a cyclic product, which is either the 1 : 2-adduct **16** or a 1 : 3-adduct **17**[40] (see Scheme 12). An exact structure elucidation was not possible, because this compound could not be freed completely of sulfur impurities without decomposition. These circumstances prevented a satisfactory elemental analysis. The mass spectrum indicated – as explained above – only the monoadduct.[40]



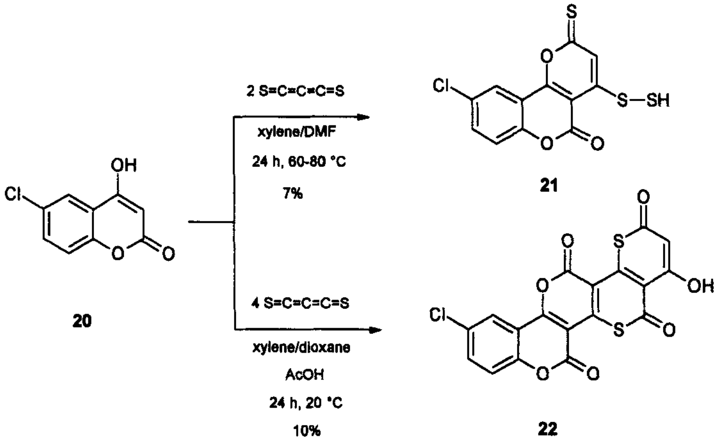
SCHEME 12 Reaction of carbon subsulfide with thiobenzamide.

2-Mercaptopyridine **18**, a 1,3-binucleophilic *N*-substituted thioamide derivative with the structure NR=CR–SH, reacted with carbon subsulfide to give a dark colored product which shows again the mass of a monoadduct. In this case, however, the purification was successful and gave the elemental analysis of a 1 : 4-adduct, namely the cross-conjugated betaine 3,5,13,15-tetrathioxo-3*H*,5*H*,13*H*,15*H*-4,6,7,14-tetrathia-12-azoniabenzo[*b*]chrysene-1-thiolate (**19**)[40] (see Scheme 13).



SCHEME 13 Reaction of carbon subsulfide with 2-mercaptopyridine.

6-Chloro-4-hydroxycoumarin **20**, having as 1,3-binucleophilic moiety the enol structure CHR=CR–OH, did not react with carbon subsulfide at room temperature. Long reaction times at 60–80 °C gave a small yield of a 1 : 1-adduct (see Scheme 14), to which the structure 9-chloro-5-oxo-2-thioxo-2*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-4-yldisulfane **21**[40] was assigned by mass spectral analysis. Attempts to obtain better yields of **21** by acid catalysis with glacial acetic acid gave a 1 : 4-adduct, to which the structure of 11-chloro-4-hydroxy-8,13-dioxa-1,6-dithia-2,5,7,14-picenetetraone **22**[40] was assigned by mass spectral and elemental analyses (see Scheme 14). It is remarkable that the exchange of the exocyclic thioxo groups against oxo groups led to higher stability, which made it easier to purify and isolate the product. Also the mass spectrum showed the real mass and not only that of a monoadduct.



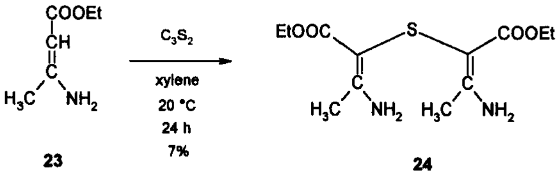
SCHEME 14 Reaction of carbon subsulfide with 6-chloro-4-hydroxycoumarin.

4.4. *Formation of Sulfanes*

The reaction of carbon subsulfide with ethyl 3-amino-2-butenoate **23** (ethyl β-aminocrotonate), which contains a 1,3-binucleophilic enamine structure $CHR{=}CR{-}NH_2$, did not lead to the expected thiopyrone or to a higher fused adduct, similar to the reactions shown in Section 4.3. Work-up of the reaction mixture by column chromatography followed by preparative thin layer chromatography gave as main product bis(2-amino-1-ethoxycarbonyl-1-propenyl) sulfide **24**[45,66] (see Scheme 15). The structure elucidation was performed by an unambigous synthesis of **24** from **23** and morpholine-*N*-sulfenyl chloride.[45,66]

4.5. *Metal Complexes*

Carbon subsulfide has found interest as a ligand for transition metals because of its diversity of behavior. It was found to serve as a

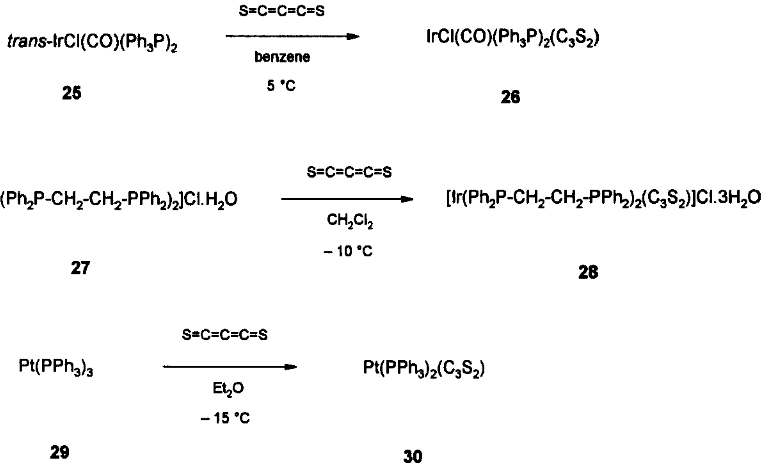


SCHEME 15 Reaction of carbon subsulfide with ethyl 3-amino-2-butenoate.

sulfur-donor ligand, by interaction via its C=S bonds in the manner of carbon disulfide and via its C=C bonds in the manner of olefin complexes.

Ginsberg *et al.*[44,67] have treated coordinatively unsaturated, low-valent platinum metal complexes with carbon subsulfide under a nitrogen or argon atmosphere. The reaction of the iridium complex **25** gives, with oxidative addition, the 1 : 1-adduct **26** (see Scheme 16).

This complex shows a strong infrared absorption at 1985 cm^{-1} which was assigned to the C=C bond of bound carbon subsulfide, which indicates that the bonding in **26** partially preserves its identity. Whereas the adduct **26** is rather unstable, changing the substituents at the phosphorus atom (in **27**) or using other metals (in **29**) leads to the more stable complexes **28** and **30** (see Scheme 16). The occurrence of infrared


$$\textit{trans}\text{-IrCl(CO)(Ph}_3\text{P)}_2 \xrightarrow[\text{benzene, } 5\,^\circ\text{C}]{\text{S=C=C=C=S}} \text{IrCl(CO)(Ph}_3\text{P)}_2\text{(C}_3\text{S}_2\text{)}$$
25 **26**

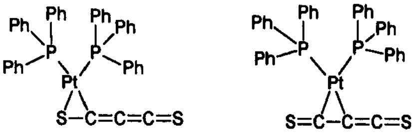
$$[\text{Ir(Ph}_2\text{P-CH}_2\text{-CH}_2\text{-PPh}_2)_2]\text{Cl.H}_2\text{O} \xrightarrow[\text{CH}_2\text{Cl}_2,\ -10\,^\circ\text{C}]{\text{S=C=C=C=S}} [\text{Ir(Ph}_2\text{P-CH}_2\text{-CH}_2\text{-PPh}_2)_2(\text{C}_3\text{S}_2)]\text{Cl.3H}_2\text{O}$$
27 **28**

$$\text{Pt(PPh}_3)_3 \xrightarrow[\text{Et}_2\text{O},\ -15\,^\circ\text{C}]{\text{S=C=C=C=S}} \text{Pt(PPh}_3)_2(\text{C}_3\text{S}_2)$$
29 **30**

SCHEME 16 Reaction of carbon subsulfide with platinum metal complexes to form 1 : 1-adducts.

absorptions at 1980–1995 cm^{-1} shows that the bonding of carbon subsulfide in all these three compounds is similar.[44,67]

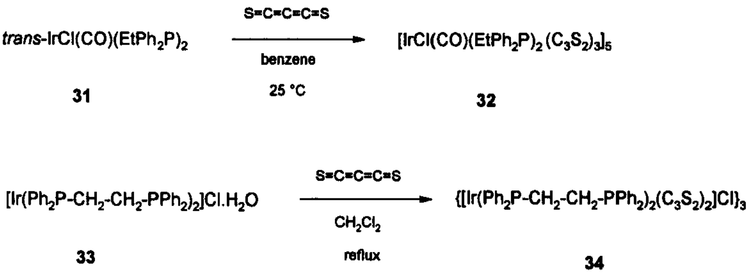
The analysis of the infrared spectra reveals that the carbon subsulfide has undergone oxidative addition to the metal. The structures **30A** and **30B** (see Scheme 17) indicate the two possible modes of oxidative addition. The authors of Refs. [44,67] favor structure **A** because of their infrared assignments.



30A **30B**

SCHEME 17 Possible modes of the oxidative addition of carbon subsulfide to platinum metal complexes.

The metal complexes **31** and **33** form adducts with more than one molecule of carbon subsulfide to give the adducts **32** and **34**[44,67] (see Scheme 18). The infrared spectra show again that oxidative addition has taken place in **32**, and probably also in **34**. The authors assume that only one molecule has reacted by oxidative addition, and then additional carbon subsulfide has interacted with the already bound molecule; this suggestion is supported by the fact that the original C=C infrared signals of 1980–1995 cm^{-1} have disappeared. Furthermore, the molecular weight of the oligoadducts is about 3–5 times of the molecular weight of the parent molecule, so that these products appear to be oligomeric.



$$\textit{trans}\text{-IrCl(CO)(EtPh}_2\text{P)}_2 \xrightarrow[\text{benzene, 25 °C}]{\text{S=C=C=C=S}} [\text{IrCl(CO)(EtPh}_2\text{P)}_2(\text{C}_3\text{S}_2)_3]_5$$

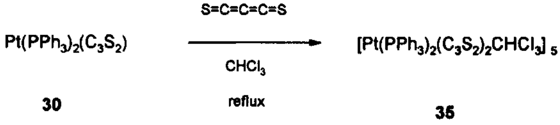
31 **32**

$$[\text{Ir(Ph}_2\text{P-CH}_2\text{-CH}_2\text{-PPh}_2)_2]\text{Cl.H}_2\text{O} \xrightarrow[\text{CH}_2\text{Cl}_2\text{, reflux}]{\text{S=C=C=C=S}} \{[\text{Ir(Ph}_2\text{P-CH}_2\text{-CH}_2\text{-PPh}_2)_2(\text{C}_3\text{S}_2)_2]\text{Cl}\}_3$$

33 **34**

SCHEME 18 Reaction of carbon subsulfide with platinum metal complexes to oligoadducts.

Addition of carbon subsulfide to the primary 1 : 1-adducts was observed when the platinum complex **30** was heated with additional carbon subsulfide. As product the 2 : 1-adduct **35**[44,67] was formed (see Scheme 19). Again the C=C infrared signal at 1995 cm^{-1} disappeared upon this addition.

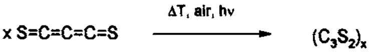


$$\underset{\mathbf{30}}{\mathrm{Pt(PPh_3)_2(C_3S_2)}} \xrightarrow[\mathrm{CHCl_3}\ \mathrm{reflux}]{\mathrm{S{=}C{=}C{=}C{=}S}} \underset{\mathbf{35}}{\mathrm{[Pt(PPh_3)_2(C_3S_2)_2CHCl_3]_5}}$$

SCHEME 19 Addition of carbon subsulfide to a 1 : 1-adduct of carbon subsulfide with a platinum metal complex.

4.6. Polymerization Reactions

The polymerization of the liquid, red colored carbon subsulfide to a black solid of the structure $(C_3S_2)_x$ (see Scheme 20) is observed when carbon subsulfide is warmed or photolyzed; other methods are the action of air, pressure, acids and bases.

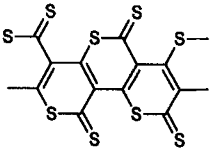


$$x\ \mathrm{S{=}C{=}C{=}C{=}S} \xrightarrow{\Delta T,\ \mathrm{air},\ h\nu} (\mathrm{C_3S_2})_x$$

SCHEME 20 Polymerization of carbon subsulfide.

First experiments were performed already by von Lengyel[1] and by Stock and Praetorius.[2] The latter observed that the reaction kinetics were those of a bimolecular reaction; no other reaction products had been formed. Polymeric $(C_3S_2)_x$ did not react with water, sodium hydroxide, hydrochloric acid or chlorine solution.

Diallo and Dixmier[43] obtained the $(C_3S_2)_x$ polymer from carbon subsulfide by heating to 70–90 °C. They found that above 400 °C decomposition of the polymer took place, and traces of carbon subsulfide and carbon disulfide could be observed. The residue consisted of carbon and sulfur. Diallo[68] stated that the infrared spectra obtained from the $(C_3S_2)_x$ polymer under exclusion of water differed from infrared spectra obtained from the $(C_3S_2)_x$ polymer which had been polymerized without any precautions. The signals of the C=S and S–C=S vibrations exhibit a shift of up to 70 cm^{-1}, which was explained by Diallo[68] by the presence of monomeric carbon subsulfide and carbon disulfide enclosed in the crystal. The crystal distances have been determined by X-ray diffraction.[43] The C=C bands showed almost the same frequencies as in the carbon suboxide polymer.[63] From these findings the structure of the $(C_3S_2)_x$ polymer has been formulated as a poly(thiopyrone) of the formula **36**[6,71] (see Scheme 21) by analogy to the structure of the $(C_3O_2)_x$ polymer.



36

SCHEME 21 Structure of the polymer $(C_3S_2)_x$.

Ginsberg *et al.*[69] synthesized the $(C_3S_2)_x$ polymer by allowing a sample of carbon subsulfide to stand at room temperature until it was completely transformed to a black solid (within several days) or by warming a sample of carbon subsulfide on a steam bath until it was mostly converted to a black solid (about 1 h). The black solid was washed with dichloromethane and dried at 25 °C in a desiccator (10^{-3} Torr); the $(C_3S_2)_x$ polymer dissolves completely in boiling 6 N sodium hydroxide to give a red-brown solution from which a brown-black solid precipitates upon acidification.

When Ginsberg *et al.*[69] applied pressure to carbon subsulfide, they obtained at high pressures (~ 14 kbar) as decomposition product, a mixture of graphite and sulfur; at ~2 kbar, carbon subsulfide polymerizes in an exothermic reaction to a $(C_3S_2)_x$ polymer of the same type as that formed at room temperature and atmospheric pressure. The infrared spectra obtained from these $(C_3S_2)_x$ polymers differ a little from those obtained by Diallo and Dixmier;[43] the band at 1000 cm^{-1} is not present in Ginsberg's[69] spectra.

Polymeric $(C_3S_2)_x$ was also detected when carbon disulfide was subjected by Agnew *et al.*[70] to a pressure of about 8 GPa. The infrared spectra are similar to that obtained by Diallo[68] including the missing 1000 cm^{-1} band mentioned above. Also photopolymerization of carbon disulfide gives the $(C_3S_2)_x$ polymer.[6,59]

5. CONCLUSION

The chemistry of carbon subsulfide, as can be seen in this review suffers from an inconvenient synthesis with its low yields. For further developments this disadvantage should be overcome. Perhaps the flash vacuum pyrolysis of S-heterocycles (see Section 3.2.3) can be developed to preparatively useful reactions.

The reactions of carbon subsulfide reveal that in all synthetic investigations – organic cyclization reactions, formation of metal complexes and polymerization reactions – a strong tendency can be observed for carbon subsulfide to give polyfused molecules by self-condensation to thiopyrones, much stronger than that observed in carbon suboxide chemistry.[63] Probably the increased nucleophilic properties of the sulfur atoms are the reason for this behavior.

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