

CYCLIC CARBONATES AND THIOCARBONATES

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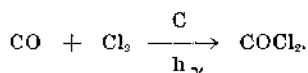
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As a compound carbonic acid exists to a slight extent in equilibrium with its decomposition products, carbon dioxide and water:



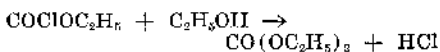
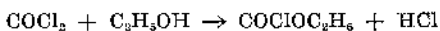
Pauling (1960:327) states that the ratio of dissolved carbon dioxide molecules to carbonic acid molecules is about 25 to 1. This would lead to a true value for the ionization constant of about 2×10^{-4} . Apparently, then, carbonic acid is somewhat stronger than acetic acid. The instability of carbonic acid can be attributed to the fact that the molecule is a gem-diol, a type normally decomposed with loss of water. In spite of the instability of the acid itself, many derivatives can be prepared through the use of the anhydride, CO_2 , the double acid chloride, phosgene, COCl_2 , and the double amide, urea, $\text{CO}(\text{NH}_2)_2$. Likewise the thioacids, monothiocarbonic acid, HOCOSH , dithiocarbonic acid, $\text{O}=\text{C}(\text{SH})_2$, and trithiocarbonic acid, $\text{S}=\text{C}(\text{SH})_2$, are unstable, but their anhydrides, carbonyl sulfide, COS , and carbon disulfide, CS_2 , are known as are the acid chloride, thiophosgene, $\text{S}=\text{CCl}_2$, and the amide, thiourea, $\text{S}=\text{C}(\text{NH}_2)_2$.

Phosgene was first prepared in 1812 by Sir Humphrey Davy by the combination of carbon monoxide and chlorine in sunlight in the presence of charcoal:

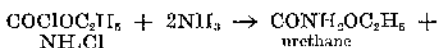


The name phosgene was chosen because the substance had its origin in light. This method is still used commercially, activated charcoal being used. The cast iron catalyst chamber is thoroughly cooled with water before the gases are admitted. About 80% conversion occurs on the first pass. In a second chamber the process is completed at elevated temperatures.

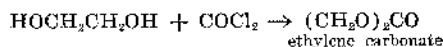
Typical of acid chlorides phosgene will react with ammonia, water, and alcohols. With a monofunctional alcohol, such as ethanol, the reaction proceeds through the chlorocarbonate (The chlorocarbonates are also named chloroformates since they are esters of the hypothetical acid, chloroformic acid, ClCOOH .) stage to the dialkyl carbonate:



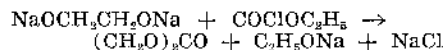
Alcohol is added to commercial grades of chloroform to remove the phosgene which results when the chloroform stands in contact with air. If the ethyl chlorocarbonate is treated with ammonia instead of excess alcohol, urethane results:



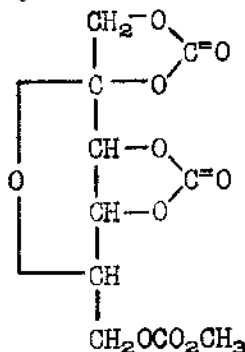
If a glycol be substituted for the monofunctional alcohol in the reaction with phosgene, a cyclic carbonate is produced:



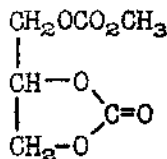
Nemirowsky (1883) was able to produce ethylene carbonate in good yield by passing a stream of phosgene through ethylene glycol at ordinary temperatures and pressures. The carbonate is also produced from ethyl chloroformate and the disodium derivative of glycol:



This method was used by Allpress and Haworth (1924) to produce sugar carbonates. For example fructose, in aqueous solution, reacts with alkyl chloroformates at 0°C. to produce sugar carbonates such as monocarbomethoxyfructose dicarbonate:



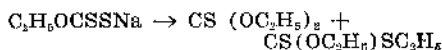
Under similar conditions glycerol yields monocarbomethoxyglycerol carbonate:



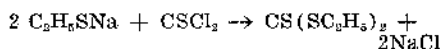
These compounds are completely

hydrolyzed by acids, alkalis, and sodium alkylates.

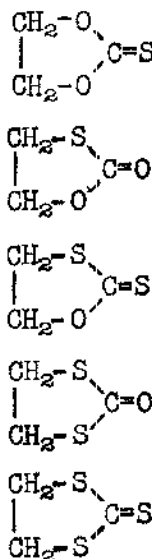
The first thiocarbonates were reported by Debus (1850) who prepared diethylthioncarbonate, $\text{SC}(\text{OC}_2\text{H}_5)_2$ by heating ethyl xanthate. Some diethylthionthiocarbonate is formed at the same time:



He made the trithiocarbonate by the action of thiophosgene on sodium ethyl mercaptide:



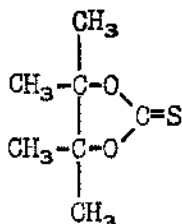
It is apparent that five different cyclic thiocarbonates can be derived from ethylene or its symmetrical derivatives:



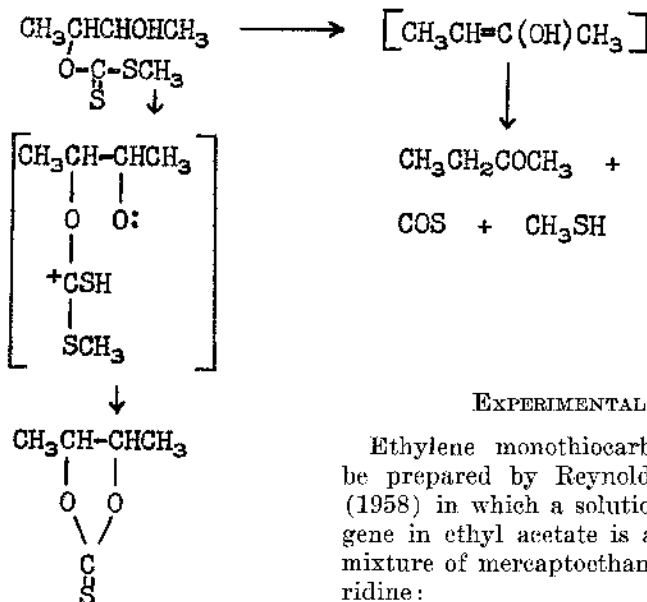
With unsymmetrical derivatives or with fused rings additional isomeric forms may be deduced.

Fomin (1935) showed that the pinacol derivative of methyl xanthate, $\text{Me}_2\text{C}(\text{OCS}_2\text{Me})\text{C}(\text{OH})\text{Me}_2$, is decomposed in the process of forma-

tion without separation of COS and with the evolution of MeSH to give the stable tetramethylethylene thio-carbonate:

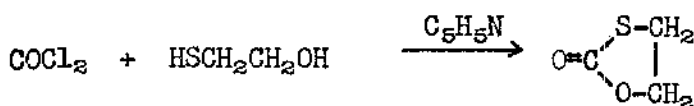


Stevens and Richmond (1941) found that the decomposition of 2,3-butylene glycol monoxanthate followed two paths, one producing methyl ethyl ketone, presumably through the enol, and the other yielding a cyclic thiocarbonate:

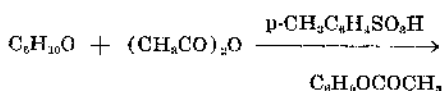


EXPERIMENTAL

Ethylene monothiocarbonate can be prepared by Reynold's method (1958) in which a solution of phosgene in ethyl acetate is added to a mixture of mercaptoethanol and pyridine:

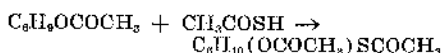


A modification of this method was used in the preparation of the two isomeric cyclohexene monothiocarbonates. Starting point for the cis isomer was cyclohexanone. Bedoukian's method (1945) was used to convert it into the enol acetate:



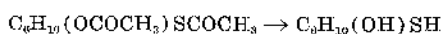
The mixture of cyclohexanone (196 g), acetic anhydride (408 g) and p-toluenesulfonic acid (2 g) was heated for 9 hours under a 10 cm column packed with Lessing rings. The acetic acid was distilled off as formed. The mixture was cooled, 200 ml of water added to decompose unchanged acetic anhydride, the oily layer was washed with water and then with 2N Na_2CO_3 solution. The ester was extracted with ether and dried. Distillation at 29-33° (0.1 mm) gave a yield of about 50%.

Thioacetic acid converted the cyclohexenyl acetate into cis-diacetyl-2-mercaptocyclohexanol:



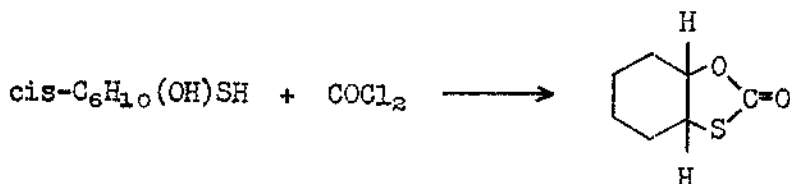
A 25 g portion of the enol acetate was placed in a flask connected to a reflux condenser and 25 g of thioacetic acid and 2.5 g of glacial acetic acid were added. After standing for 2 hours the mixture was heated on the steam bath for 1.5 hours. Fractional distillation at 1.5 mm pressure gave 20 g boiling at 115-118°.

The diester was hydrolyzed to the cis-2-mercaptocyclohexanol by a solution of hydrogen chloride in methanol:



Hydrogen chloride gas was passed into methanol until the concentration, as determined by titration with 2N NaOH, was 16.9 g per 100 ml. A 5 g portion of the diester was mixed with 20 ml of methanol and 20 ml of the HCl solution. After standing 5 days the methanol and hydrogen chloride were removed under reduced pressure. The hydroxythiol distilled at 89-91° under a pressure of 8 mm. The yield was 70%.

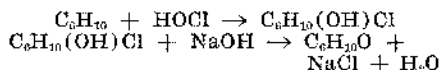
Condensation of the cis-2-mercaptocyclohexanol with phosgene led to the cis-cyclohexane monothiocarbonate:



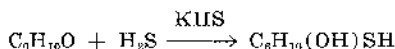
In a 100 ml flask were placed 1.6 g of the hydroxythiol, 8 ml of toluene, and 3 g of pyridine. The flask was cooled in an ice bath and 9.75 g of a 12.5% solution of phosgene in toluene added. A white precipitate of pyridine hydrochloride appeared immediately. After 30 minutes a second 9.75 g portion of the phosgene solution was added. At the end of an hour 10 ml of water was added to decompose any excess phosgene. A nitroprusside test for thiol sulfur was negative. The product was extracted with chloroform, washed twice with 25 ml portions of 2N HCl and once with water. After drying the chloroform solution and removing the solvent under reduced pressure, the product was obtained as a colorless oil boiling between 88 and 90° at a pressure of 10⁻⁴ mm. Analysis: found C = 53.22%, H = 6.40%, S = 20.23%. C₇H₁₀O₂ requires C = 53.15%, H = 6.37%, S = 20.26%. U.V. spectrographic data:

$$\epsilon = 4187, \lambda_{\max} = 204.4 \mu$$

The trans isomer was made from cyclohexene which was first converted into the epoxide by the method of Coleman and Johnstone (1941).

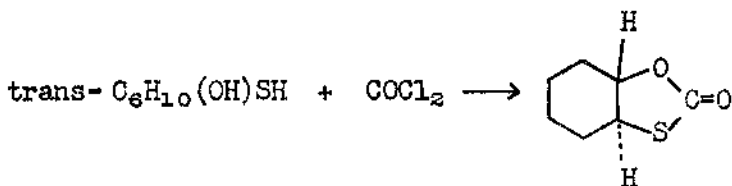


Cyclohexane oxide treated with H₂S and KHS led to the trans-2-cyclohexanol:



A solution of 5.6 g of KOH in 40 ml of ethanol was saturated with H₂S while the mixture was kept at 0°C in an ice bath. 9.8 g of cyclohexene oxide was then added to the KSH solution. Hydrogen sulfide was bubbled into the mixture. The temperature rose to 40° due to the heat of the reaction but had returned to room temperature after 30 minutes. Water was added to the pale yellow reaction mixture and the excess KOH was neutralized with 100 ml of N H₂SO₄. H₂S was evolved and a white precipitate appeared which dissolved in excess water. The product was extracted with chloroform and the chloroform solution dried with anhydrous MgSO₄. After removal of the chloroform under reduced pressure the product distilled as a viscous water-white liquid at 71-72° (1.5 mm).

The trans-cyclohexane monothio-carbonate was obtained from the trans-2-mercaptocyclohexanol by the use of phosgene:



A 2.13 g portion of the hydroxythiol was placed in a 100 ml flask with 4 g of pyridine and 10 ml of toluene. The mixture was cooled in an ice bath and 13 g of a 12.5% solution of phosgene in toluene added. After standing 50 minutes another 13 g portion of the phosgene solution was added. The excess of phosgene was decomposed with 15 ml of water and the product extracted with toluene. The toluene solution was washed twice with 25 ml portions of 2N HCl and once with 25 ml of water. The toluene solution was dried with $MgSO_4$ and the solvent removed under reduced pressure. The product distilled at 80-86° under a pressure of 5×10^{-3} mm. On a second run the material crystallized in the condenser to give colorless needles melting at 27°. Analysis: found C = 53.10%, H = 6.32%, S = 20.25%. $C_7H_{10}O_2S$ requires C = 53.15%, H = 6.37%, S = 20.26%. U.V. spectrographic data: $\epsilon = 8184$, $\lambda_{max} = 203.6$ m μ

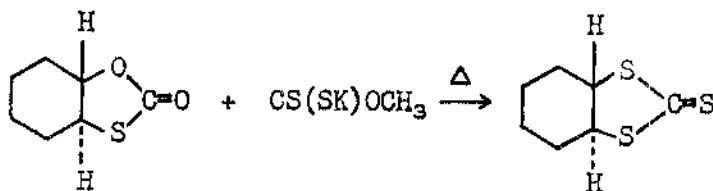
The trans isomer is readily converted into the trithiocarbonate by treatment with potassium methyl xanthate (potassium methoxymethanethionothiolate), $CS(SK)OCH_3$, on heating under reflux for 3 hours at 75°C.

The yield was 95% of the theoretical. Under similar treatment the cis isomer underwent considerable decomposition but did yield a few small crystals of the bright yellow trithiocarbonate.

Evidence that no inversion occurs during condensation of the mercapto-cyclohexanols with phosgene is largely circumstantial. First, trans isomers almost universally melt higher than their cis equivalents. The trans cyclohexanemonothiocarbonate crystallized in the condenser during distillation while the cis form could not be made to crystallize even by cooling in liquid nitrogen or storage in the refrigerator for several days. Second, the study of thermal stability, which will be covered in a later paper, confirmed the belief that the solid isomer was, indeed, the trans form.

SUMMARY

Two new cyclic monothiocarbonates have been prepared from the isomeric 2-mercaptocyclohexanols by treatment with phosgene. The cis isomer is a colorless oil while the trans isomer is a crystalline solid. The trans isomer is easily converted



m.p. 171.5 - 173°

in almost a theoretical yield into the trithiocarbonate by heating with potassium methyl xanthate.

ACKNOWLEDGMENTS

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