



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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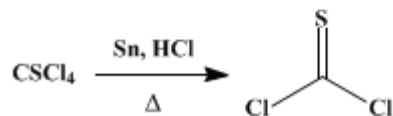
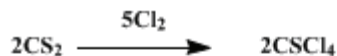
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.506 (1941); Vol. 6, p.86 (1926).

THIOPHOSGENE



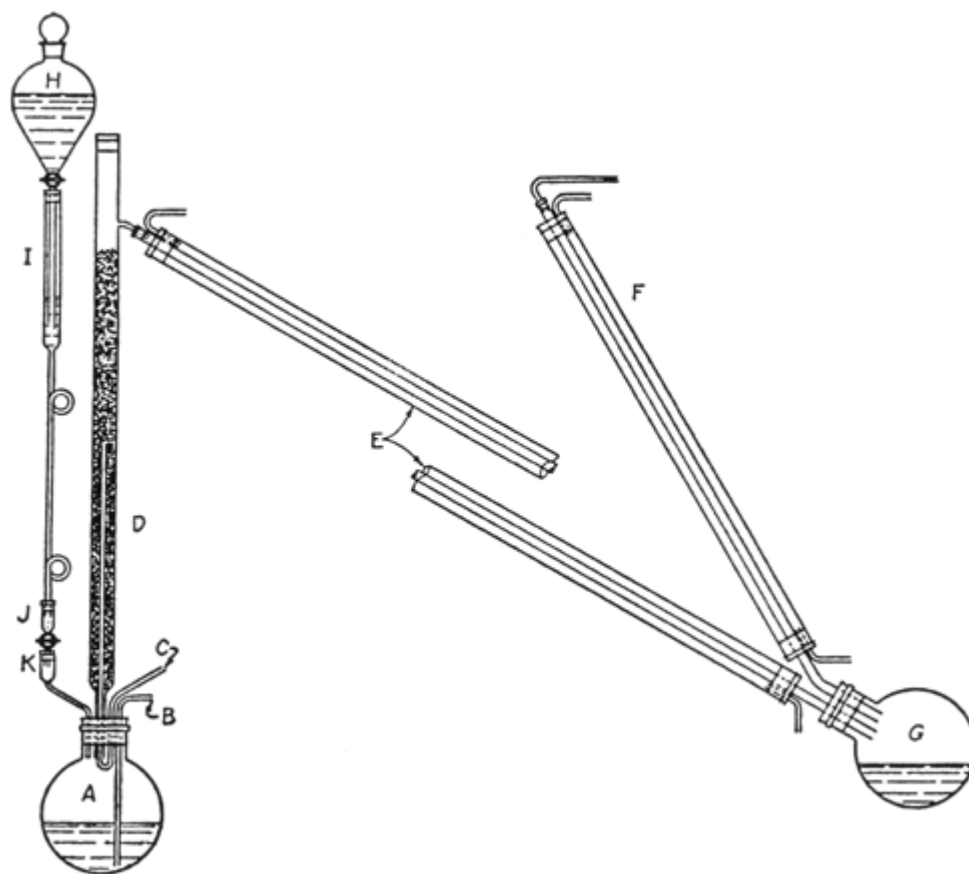
Submitted by G. Malcolm Dyson
Checked by Frank C. Whitmore and A. M. Griswold.

1. Procedure

(A) *Preparation of Thiocarbonyl Perchloride.*—In a 5-l. bottle arranged for cooling by running water is placed 500 g. (398 cc., 6.58 moles) of dry carbon disulfide (Note 1) to which 0.5 g. of iodine has been added. Dry chlorine is passed into the cooled carbon disulfide at such a rate that the temperature does not rise above 25°, until the liquid weighs 1770 g. (17.9 moles of chlorine) (Note 2). The time required is about forty hours. The product, a mixture of impure thiocarbonyl perchloride and sulfur chloride, is a deep red liquid.

The apparatus illustrated in Fig. 27 is assembled, in a large hood if possible (Note 3). A is a 5-l. round-bottomed flask heated by a large ring burner and provided with a specially treated four-holed cork stopper covered with tin foil (Note 4). To these holes are fitted the column D, the tube B reaching to the bottom of A, the specially bent tube C reaching up the inside of D, and the tube K connected with the tubes leading to the 2-l. separatory funnel H, so that the distance between the stopper of A and the stopcock of H is at least 100 cm. The bottom of the column D is of 20-mm. bore; the main portion is of 30 mm.

Fig. 27.



The side arm should be at least 85 cm. above the stopper of A. The tube C should reach about half way up the inside of the column D. The column is filled with pieces of 3-mm. glass tubing about 5 mm. long. Its top is provided with a cork covered with tin foil and fitted fairly loosely so as to blow out in case of a clogging of the apparatus. It should be held by a wire to prevent its being blown out entirely. Tubes B and C are connected with a steam line or steam generator of large capacity. The separatory funnel H is placed at the highest available level (Note 5) and connected with the tubes I, J, and K in such a manner as to secure a pressure of liquid sufficient to more than balance the steam pressure (Note 6). E and F are specially constructed condensers of unusual length (160 cm. and 85 cm., respectively) and bore (40 mm.) made from large glass tubing and rubber stoppers (Note 7). The top of condenser F is connected to a good draft chamber or to a gas-absorption trap (Fig. 7 on p. 97). G is a 5-l., or better, a 12-l. round-bottomed flask which is used as a receiver.

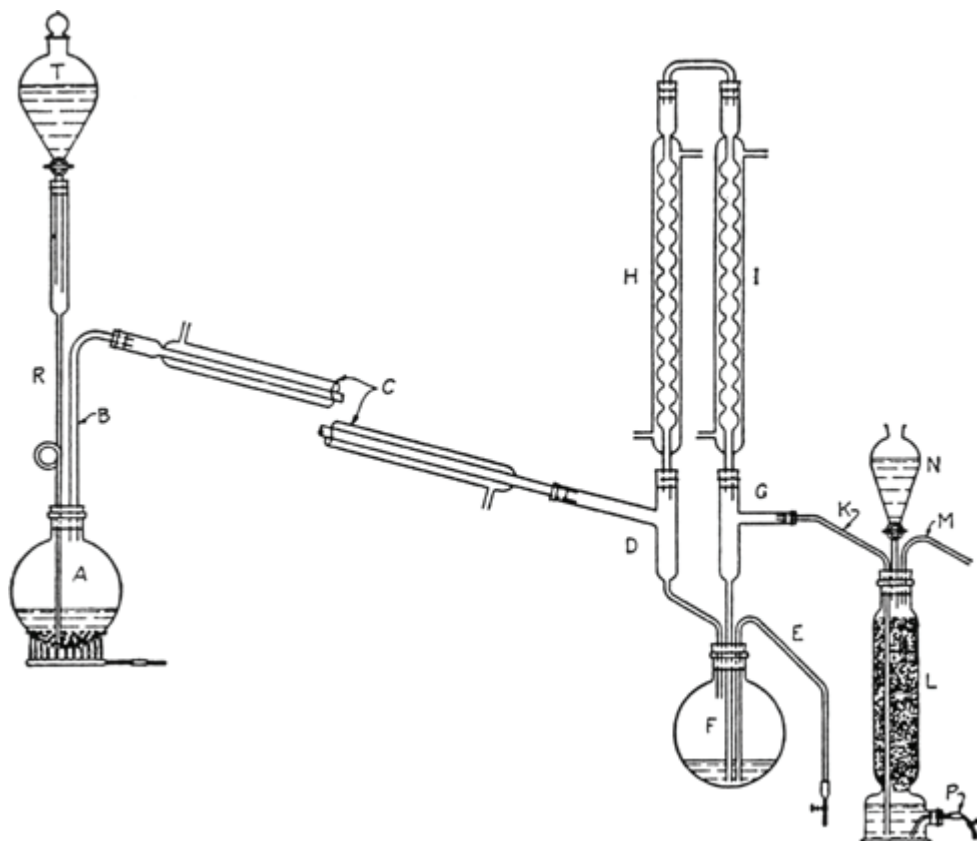
The crude chlorinated mixture is steam-distilled in this special apparatus to obtain thiocarbonyl perchloride and to decompose the sulfur chloride. In flask A is placed 1210 cc. of water which is heated to boiling by means of the ring burner. Steam is passed in through tubes B and C. The chlorinated mixture is placed in the separatory funnel H, and the connecting tubes are filled with the liquid which is allowed to pass into A at about 5 drops per second (Note 8). Sulfur begins to separate in the column and in the condensers. The steam distillation requires about five hours and gives 10–12 l. of distillate consisting of water, sulfur, and a heavy red oil. The water is decanted and the rest of the mixture is filtered by suction through glass wool. The oil is separated and dried over about 10 g. of calcium chloride.

The crude, dry thiocarbonyl perchloride is distilled through an efficient 60-cm. column (Note 9). The distillate below 140° is discarded. The fraction boiling at 140–155° at atmospheric pressure amounts to about 600 g. The boiling point of pure thiocarbonyl perchloride is 149°.

(B) *Reduction of Thiocarbonyl Perchloride to Thiophosgene.*—The apparatus illustrated in Fig. 28 is assembled. A is a 5-l. round-bottomed flask heated by a ring burner and provided with a two-holed,

specially treated cork (Note 4) carrying tube B of about 40-cm. length connected with condenser C of about 115-cm. length, and tube R which conveys the perchloride from the separatory funnel T (Note 6). R is 6-mm. tubing of about 90-cm. length and must reach to the bottom of A. D and G are specially blown connecting tubes, D reaching through the cork of F and G reaching to the bottom of the 5-l. flask, F. Each arm of D is about 20 cm. long and of 2-cm. bore. The vertical arm of G is of about 3-cm. bore and its side arm of about 1-cm. bore. H and I are efficient bulb condensers at least 60 cm. long. F is provided with siphon E for removing the product. L is a tall tower (about 50 cm. in length) packed with short pieces of glass tubing alternating with layers of glass wool. Its stopper carries the tube K reaching to the bottom of the tower, a separatory funnel, and an exit tube M leading to the draft. P is a siphon for removing the xylene wash liquid.

Fig. 28.



In the flask A are placed 750 g. (6.3 atoms) of granulated tin (Note 10) and 1500 cc. of commercial hydrochloric acid (about 28 per cent). The mixture is heated until the action is vigorous. The thiocarbonyl perchloride is run in from the funnel T (Note 11). The resulting reaction is very violent. The vapors are condensed in the series of condensers and in the scrubber L through which xylene is allowed to flow slowly from the separatory funnel N. Most of the crude thiophosgene collects in F, although a small amount is obtained from the distillation of the xylene wash liquid.

The crude thiophosgene is separated and dried with about 10 g. of calcium chloride, and fractionated with a good column. Very little distils below 73°. The fraction boiling at 73–76° at atmospheric pressure is pure thiophosgene and amounts to about 180 g. (24 per cent of the theoretical amount) (Note 12). The fraction above 76° is largely thiocarbonyl perchloride and may be again reduced or added to the reduction in a subsequent run.

2. Notes

1. Ordinary commercial carbon disulfide was used after drying over calcium chloride.
2. Any great excess of chlorine should be avoided as it favors the formation of carbon tetrachloride.

Practically as good yields have been obtained by using only about three-fourths the amount of [chlorine](#) indicated.

3. The vapors formed in the experiment are very objectionable. It is even advisable to transfer the liquids from one vessel to another by suction rather than by pouring in order to avoid the irritating and lachrymatory effects of the vapors.

Decided care should be exercised in the handling of [thiophosgene](#) because of its high toxicity.

4. It is advisable to saturate all corks with [sodium silicate](#) solution after fitting and boring them ([Note 1 on p. 17](#)). They are then covered with lead foil, wired in, and coated with shellac.

5. As long a column of liquid as possible is used to overcome the tendency for steam to work back up the inlet tube. If this happens, the [sulfur](#) formed is likely to clog the tube. This can be avoided by proper manipulation of the stopcock J.

6. The backing of steam up the inlet tube is one of the most serious difficulties in the experiment. This can be avoided if the tube I (Fig. 27) is once filled with the perchloride.

7. No ordinary condenser was found sufficiently effective to condense the vapors and not be clogged by the [sulfur](#). The specially constructed wide condensers are absolutely necessary.

8. If the addition is much more rapid than this, not all the [sulfur chloride](#) is decomposed.

9. The distillation of the crude perchloride is necessary to remove [carbon tetrachloride](#) and other low-boiling impurities which could not later be separated from the [thiophosgene](#) by distillation.

10. The [tin](#) used should be in fairly large granules; otherwise the reaction is likely to become too violent. In general, the faster the reduction the better the yield of [thiophosgene](#). In a few cases yields of 50–60 per cent have been obtained.

11. The time of addition of the perchloride should be made as short as possible consistent with safety. In runs with the above amounts of materials, the time of the addition was about ten minutes. It may again be emphasized that the yield in this reaction depends largely on the skill of the operator in running the reduction as rapidly as possible.

12. As has been stated, larger yields are occasionally obtained, but they cannot be depended on.

3. Discussion

[Thiophosgene](#) can be prepared by the reduction of thiocarbonyl perchloride.¹ A simpler method for preparing the intermediate thiocarbonyl perchloride has been described.² Compare Autenrieth and Hefner, Reference 1.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 1, 165](#)

References and Notes

1. Klason, *Ber.* **20**, 2376 (1887); Johnson and Hemingway, *J. Am. Chem. Soc.* **38**, 1551 (1916); Frankland, Challenger, and Webster, *J. Soc. Chem. Ind.* **39**, 256 (1920); de Fazi, *Gazz. chim. ital.* **53**, 175 (1923) [*C. A.* **17**, 2402 (1923)]; **54**, 251 (1924) [*C. A.* **18**, 3328 (1924)]; Guglielmelli, Novelli, Ruiz, and Anastasi, *Anales asoc. quím. argentina*, **15**, 337 (1927) [*Chem. Zentr.* II, 987 (1928)]; Autenrieth and Hefner, *Ber.* **58**, 2153 (1925).
2. Helfrich and Reid, *J. Am. Chem. Soc.* **43**, 591 (1921).

Appendix

Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

Thiocarbonyl Perchloride

calcium chloride (10043-52-4)

hydrochloric acid (7647-01-0)

sodium silicate

carbon tetrachloride (56-23-5)

tin (7440-31-5)

sulfur (7704-34-9)

iodine (7553-56-2)

chlorine (7782-50-5)

carbon disulfide (75-15-0)

Thiophosgene (463-71-8)

xylene (106-42-3)

sulfur chloride