Organic Syntheses

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of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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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.

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METHANESULFINYL CHLORIDE

[Method I]

$$CH_3S\text{—}SCH_3 \xrightarrow[-10\text{ to }0\ ^\circ C]{Cl_2,\ Ac_2O} 2\ \ CH_3S\text{—}Cl$$

$$CH_3S\text{—}Cl \xrightarrow{Cl_2} CH_3SCl_3$$

$$CH_3SCl_3 \xrightarrow{Ac_2O} 2\ \ CH_3S(O)Cl$$

Submitted by Irwin B. Douglass and Richard V. Norton[1].
Checked by R. D. Thompson and Henry E. Baumgarten.

1. Procedure

In a 500-ml., three-necked flask, fitted with an efficient sealed stirrer, a gas inlet tube extending within 1 in. of the reaction mixture but not below its surface, a gas outlet tube connected to a calcium chloride tube, and a low-temperature thermometer to register the temperature of the reaction mixture, are placed 23.55 g. (0.25 mole) of freshly distilled methyl disulfide (Note 1) and 51.05 g. (0.5 mole) of acetic anhydride (Note 2). The reaction flask is then partially immersed in a bath of acetone cooled by dry ice until the internal temperature has reached 0° to −10°. The temperature is maintained within these limits throughout the reaction (Note 3). The reaction is best carried out in a well-ventilated hood.

Chlorine is passed into the well-stirred mixture at such a rate that the temperature is controlled between 0° and −10°. The progress of the reaction can be followed by color changes. At first the mixture turns yellow, then reddish as methanesulfenyl chloride (CH_3SCl) accumulates but gradually the color fades, and the mixture may become colorless. The addition of chlorine is terminated when a faint greenish-yellow color indicates an excess of chlorine (Note 4).

The reaction mixture is then transferred (Note 5) with a few fresh chips of porous plate to a distilling flask having a thermometer well, and the flask is fitted to a 12- to 18-in. Vigreux column and vacuum distillation apparatus. The fraction collector of the latter is connected through a trap cooled in an acetone-dry ice bath and a safety trap to a water pump. The cold trap must have sufficient capacity to contain, without backing up, all the acetyl chloride formed in the reaction.

The pressure is gradually decreased without heating the flask. The excess chlorine rapidly escapes and at 15 mm. the acetyl chloride boils smoothly below 0°. No heat is applied until most of the acetyl chloride has been removed (Note 6). Heat is then gradually increased until at 47–48° (15 mm.) the methanesulfinyl chloride distills as a nearly colorless liquid with n_D^{25} 1.500 (lit.[2] n_D^{25} 1.5038). Its nmr spectrum shows a single peak at δ 3.33 ppm with no sign of a singlet at δ 3.64 ppm, the frequency characteristic of methanesulfonyl chloride. The yield is 41–42 g. (83–86%) (Note 7).

[Method II]

$$CH_3SSCH_3 + 3Cl_2 \longrightarrow 2CH_3SCl_3$$

$$CH_3SCl_3 + CH_3CO_2H \longrightarrow CH_3SOCl + CH_3COCl + HCl$$

Submitted by Irwin B. Douglass and Basil Said Farah[1].
Checked by Melvin S. Newman, J. T. Golden, and W. N. White..

1. Procedure

In a 1-l. three-necked flask, fitted with an efficient sealed stirrer, a gas inlet tube extending within 1 in. of the reaction mixture but not below its surface, and a gas outlet tube leading through a trap cooled in a dry ice-acetone bath to a hydrogen chloride absorption system (Note 8), are placed 94.2 g. (1 mole) of methyl disulfide (Note 9) and 120 g. (2 moles) of glacial acetic acid. The reaction flask is then surrounded by a bath of acetone cooled by dry ice until the internal temperature has reached 0° to −10°. The temperature is maintained within these limits throughout the reaction (Note 10) except that, toward the end, the temperature should be kept at −10° to −15° to minimize the escape of hydrogen chloride which might carry with it unreacted chlorine. The entire reaction is best carried out in a well-ventilated hood.

Three moles of chlorine (212.7 g.) is condensed in a tared flask cooled by a dry ice-acetone bath (Note 11). This flask is then connected to the gas inlet tube of the chlorination apparatus, and the cooling bath surrounding the chlorine container is removed. After about 2 hours the chlorine has all been absorbed by the reaction mixture (Note 12).

When the last of the chlorine has been added, the cooling bath is removed and, while vigorous stirring is continued (Note 13), the reaction mixture is allowed slowly to warm to room temperature. During this period there is a vigorous evolution of hydrogen chloride. The flask is finally warmed to 35° to facilitate the escape of more hydrogen chloride.

The reaction mixture and contents of the cold trap and then transferred (Note 14) to a 500-ml. distilling flask attached through a short fractionating column to a water-cooled condenser which is connected in series to a receiver, a trap cooled in a dry ice-acetone bath, and a hydrogen chloride absorption trap which may later be attached to a water pump. The mixture is then distilled until the pot temperature reaches 100° and practically all of the acetyl chloride has been driven over.

The residue, consisting chiefly of methanesulfinyl chloride, is then cooled immediately to 20° or lower and transferred to a 250-ml. flask and distilled through the same equipment under reduced pressure to remove the remaining acetyl chloride and other lower-boiling impurities. As the pot temperature begins to rise, a yellow intermediate fraction is collected very slowly until the distillate and pot temperatures are within 3° of each other (Note 15). At this point the distillation is temporarily discontinued while the accumulated acetyl chloride (Note 16) is removed from the cold trap and the receiver for the main product is attached. On resuming distillation the main product should come over within a 5° boiling range, and the distillation and pot temperature should remain within 2° of each other until the major part of the product has distilled. The yield is 161–177 g. (82–92%) of straw-colored or yellow product boiling at 55–59° (40 mm.) and having n_D^{25} 1.500–1.501 (Note 7).

2. Notes

1. The submitters used methyl disulfide obtained from the Crown Zellerback Corporation, Chemical Products Division, Camas, Washington, which was dried and redistilled. The fraction boiling at 108–109° was used. The checkers used methyl disulfide obtained from the Aldrich Chemical Co., Inc.
2. The success of the reaction is closely related to having stoichiometric quantities of reagents. An excess of disulfide will produce a colored product due to the presence of methanesulfenyl chloride or products from the decomposition of methylsulfur trichloride. An excess of acetic anhydride will give a problem of purification during distillation, or if chlorine is also in excess, will lead to the formation of methanesulfonyl chloride.[3]
3. The reaction of acetic anhydride with methylsulfur trichloride is temperature dependent. If the chlorination is carried out at too low a temperature (>−20°), solid methylsulfur trichloride separates as white crystals which may cause the reaction mixture to become semi-solid. At 0° to −10°, however, no solid trichloride is observed.
4. At the colorless stage, the weight of the reaction mixture indicates that a stoichiometric quantity of chlorine has been added. In some preparations, a colorless condition is not achieved and one depends on the color of excess chlorine to indicate the end of the reaction. Excess chlorine does not seem to affect the quality of the product. An alternative to depending on the color change to determine the end of the

reaction is to condense the calculated weight of chlorine in a tube and allow it to evaporate quantitatively into the reaction mixture.

5. Because of the unpleasant nature of methanesulfinyl chloride, acetyl chloride, and chlorine, the transfer should be made in the hood.

6. It is not necessary to empty the acetyl chloride from the cold trap until after the distillation is complete. Great care must be taken, however, to provide an intervening safety trap so that no water from the pump can back up into the trap holding the acetyl chloride.

7. Pure methanesulfinyl chloride boils at 48° (22 mm.) and 59° (42 mm.) and has n_D^{25} 1.5038, d_4^0 1.4044 and d_4^{25} 1.3706. On standing at room temperature, it slowly decomposes with the liberation of hydrogen chloride. It should not be stored for a long period in a tightly sealed container.

8. The hydrogen chloride absorption system must be of such design that there is no possibility for water to suck back into the reaction flask after a sudden surge of escaping hydrogen chloride.

9. The methyl disulfide was obtained from the Crown Zellerbach Corporation, Chemical Products Division, Camas, Washington, and redistilled. The 108–109° boiling fraction was used.

10. Crystalline acetic acid separates at first but redissolves as the reaction progresses.

11. The flask should be full of chlorine gas when the tare weight is taken. The success of this preparation depends in large measure on the use of stoichiometric quantities of all reagents. An excess or deficiency of any one will lead to an impure product and will greatly complicate the problem of purification.[2]

12. The white solid which collects inside the upper part of the flask is methylsulfur trichloride. This must be washed down with the cold reaction mixture before the flask warms to room temperature. The progress of the chlorination is accompanied by definite color changes. When one-third of the chlorine has been added, the reaction mixture is a deep reddish orange color which gradually fades as more chlorine is added until at the end the color should be a pale golden yellow or light straw color.

13. Vigorous stirring is necessary to prevent loss of material through too rapid escape of hydrogen chloride.

14. Since both methanesulfinyl and acetyl chlorides are unpleasant materials and the reaction mixture still contains much hydrogen chloride, all transfers should be made in the hood.

15. The difference between the distillation and pot temperature is closely related to the success of this preparation. If the specified weights of reactants and temperatures are employed a 3° temperature difference should be reached before the yellow intermediate fraction, probably containing methanesulfenyl chloride, chloromethanesulfenyl chloride, and acetic acid, has attained a volume of 10 ml. Toward the end of the distillation the pot temperature may begin to rise owing to the presence in the residue of methanesulfonyl chloride (b.p. 63°/20 mm., 72°/31 mm., 82°/48 mm.), methyl methanethiolsulfonate (b.p. 115°/15 mm.) or both. The residue at the end of the distillation should amount to less than 10 ml.

16. The acetyl chloride obtained is yellow in color, probably because of the presence of the sulfenyl chlorides mentioned above. The addition of cyclohexene will discharge the color (although a darker color develops later) and redistillation then yields a stable water-clear product. The yield of acetyl chloride varies from 60% to 85%, depending on the care with which liquids are transferred and the vapors are trapped. The amount of sulfinyl chloride which may be recovered by redistilling the acetyl chloride fraction does not justify the time required.

3. Discussion

Alkanesulfinyl chlorides have been prepared by the action of thionyl chloride on alkanesulfinic acids[4,5] and by solvolysis of alkylsulfur trichlorides with water, alcohols, and organic acids.[2] Method II is an earlier procedure of the submitters,[6] which appears to be general for the preparation of sulfinyl chlorides in either the aliphatic or the aromatic series and is based on an improvement in the solvolysis method whereby the use of inert solvent is eliminated and the reaction is carried out in a one-phase system. In the submitters' laboratory this procedure has been supplanted by Method I which is superior to any of those previously employed in that the reaction is carried out in a homogeneous medium without the formation of hydrogen chloride gas. An adaptation of the present method is to chlorinate a mixture of a thiolester and acetic anhydride.[7] The latter modification is especially effective in the preparation of α-toluenesulfinyl chloride.

The present method seems to be general for the preparation of most sulfinyl chlorides in either the aliphatic or aromatic series. Benzyl and *t*-butyl disulfides, however, do not yield sulfinyl chlorides by this method because chlorine appears to cleave the carbon-sulfur rather than the sulfur-sulfur bonds.

Sulfinyl chlorides are highly reactive and unstable compounds. Methanesulfinyl chloride, at room temperature, disproportionates into methanesulfonyl and methanesulfenyl chlorides. It should *not* be stored in a sealed container at room temperature for a long period.[8] *Aromatic sulfinyl chlorides should not be distilled* because they have been known to explode on heating. They can, however, be prepared by the present method.

4. Uses of Methanesulfinyl Chloride

The utility of methanesulfinyl chloride lies in its great activity as a chemical intermediate. Through its ready hydrolysis, it serves as a convenient source of methanesulfinic acid. It reacts at low temperatures with aromatic amines to form sulfinamides, and with alcohols to form sulfinate esters. When it is hydrolyzed in the presence of an equimolar quantity of a sulfenyl chloride, a triolsulfonate ester is produced.

References and Notes

1. University of Maine, Orono, Maine.
2. I. B. Douglass and D. R. Poole, *J. Org. Chem.*, **22**, 536 (1957).
3. I. B. Douglass and R. V. Norton, *J. Org. Chem.*, **33**, 2104 (1968).
4. J. von Braun and K. Weissbach, *Ber.*, **63**, 2836 (1930).
5. A. Meuwsen and H. Gebhardt, *Ber.*, **69**, 937 (1936).
6. I. B. Douglass and B. S. Farah, *J. Org. Chem.*, **23**, 330 (1958); *Org. Syntheses*, **40**, 62 (1960).
7. M. L. Kee and I. B. Douglass, *Org. Prep. Proced.*, **2**, 235 (1970).
8. I. B. Douglass and D. A. Koop, *J. Org. Chem.*, **29**, 951 (1964).

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

sulfinyl chloride

hydrogen chloride (7647-01-0)

acetic acid (64-19-7)

acetic anhydride (108-24-7)

acetyl chloride (75-36-5)

thionyl chloride (7719-09-7)

Cyclohexene (110-83-8)

chlorine (7782-50-5)

Methanesulfonyl chloride (124-63-0)

methyl disulfide (624-92-0)

Methanesulfinyl chloride (676-85-7)

methanesulfenyl chloride (5813-48-9)

methylsulfur trichloride

methyl methanethiolsulfonate (2949-92-0)

α-toluenesulfinyl chloride

methanesulfinic acid