A Publication
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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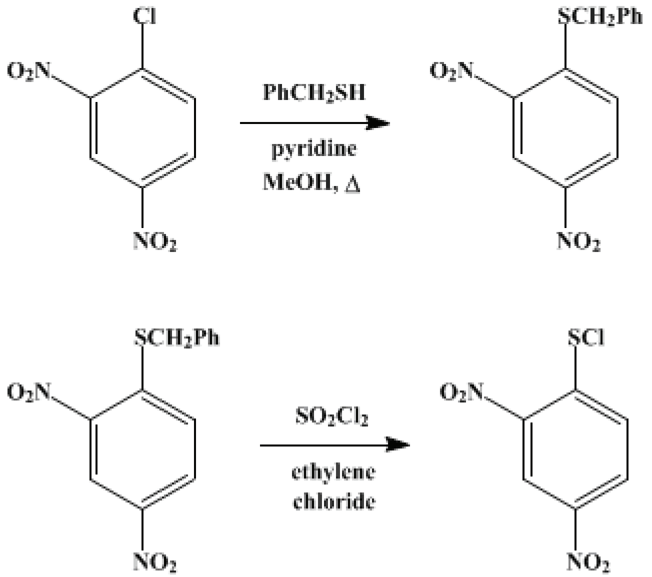
2,4-DINITROBENZENESULFENYL CHLORIDE

[Benzenesulfenyl chloride, 2,4-dinitro-]



Submitted by Norman Kharasch and Robert B. Langford[1].
Checked by D. C. Dittmer and B. C. McKusick.

1. Procedure

Caution! Both steps should be carried out in a good hood.

A. *2,4-Dinitrophenyl benzyl sulfide*. The apparatus consists of a 1-l., three-necked, round-bottomed flask equipped with a sealed mechanical stirrer and a reflux condenser. In it are placed 202 g. (1.00 mole) of 2,4-dinitrochlorobenzene (m.p. 50–52°) *(Caution! A skin irritant),* 400 ml. of methanol, 124 g. (1.00 mole) of benzyl mercaptan, and 87 g. (85 ml., 1.10 moles) of pyridine. The mixture is heated at the reflux temperature with stirring for 16 hours or more (Note 1) and cooled to 0°. The 2,4-dinitrophenyl benzyl sulfide that precipitates is separated by filtration, washed with two 250-ml. portions of ice-cold methanol, and dried at 60–80°. The sulfide, a yellow crystalline solid that melts at 128–129°, weighs 235–250 g. (81–86%) (Note 2). It may be used in the next step without further purification.

B. *2,4-Dinitrobenzenesulfenyl chloride*. Dry 2,4-dinitrophenyl benzyl sulfide (232 g., 0.80 mole) and 400 ml. of dry ethylene chloride are placed in a 2-l., one-necked, round-bottomed flask equipped with a stirrer (Note 3). Sulfuryl chloride (119 g., 0.88 mole) (Note 4) is added to the resulting suspension at room temperature. A mildly exothermic reaction causes the solid to dissolve quickly, usually within 1 to 2 minutes, with a temperature rise of 10–15° (Note 5). The resulting clear yellow solution is concentrated to an oil by heating under aspirator vacuum on a steam bath (Note 6). *(Caution! Do not heat with gas or electricity because the product, like many nitro compounds, can explode if overheated.)* The residual oil is cooled to 50–60°, and 3–4 volumes of dry petroleum ether (b.p. 30–60°) are added with vigorous handswirling. The oil quickly crystallizes. The mixture is cooled to room temperature and filtered to separate 2,4-dinitrobenzenesulfenyl chloride as a yellow crystalline solid. The sulfenyl chloride is washed well with dry petroleum ether and dried at 60–80° (Note 7); weight 150–170 g. (80–90%); m.p. 95–96° (Note 8), (Note 9).

2. Notes

1. After 2 or 3 hours, solid product usually appears in the reaction mixture.
2. When practical grade 2,4-dinitrochlorobenzene (m.p. 46–47°) is substituted, a product of equally good quality (m.p. 128–129°) is obtained, but the yield is only 70–75%.
3. All materials and equipment used in Step B of this procedure must be completely dry to avoid loss of product by hydrolysis. The checkers found, however, that the reaction may be carried out open to the air without loss of yield.
4. Practical grade sulfuryl chloride, obtained from Matheson, Coleman and Bell, gives satisfactory results.
5. The 2,4-dinitrophenyl benzyl sulfide normally undergoes cleavage at room temperature without the addition of a catalyst. If the reaction does not occur spontaneously, the mixture may be warmed gently and/or one drop of dry pyridine may be added to initiate the reaction.
6. Rotary or other distillation equipment with metal parts should not be used in concentrating the reaction mixture because not only will the corrosive vapors damage the equipment, but also the resulting metal salts will discolor and partially decompose the product. The solution should not be heated any longer than is necessary to concentrate it; excessive heating gives a darkcolored product.
7. The product should not be dried longer than is necessary for it to reach constant weight, or there may be partial decomposition.
8. The product obtained by this procedure is pure enough for most purposes. Its melt, however, is faintly cloudy. A product of high purity, giving a clear melt, can be obtained by recrystallization from about 15 ml. of dry carbon tetrachloride per gram of sulfenyl chloride. When stored in a sealed brown bottle with a plastic cap (no metal!), the sulfenyl chloride is stable for years.
9. 2,4-Dinitrobenzenesulfenyl bromide may be similarly prepared by refluxing 2,4-dinitrophenyl benzyl sulfide with the equivalent amount of bromine in 5 parts of dry carbon tetrachloride. As it is less stable than the chloride, losing bromine if overheated, it should be concentrated on a 40° water bath under vacuum. When worked up in the same manner as the chloride, the product usually contains some *bis*-(2,4-dinitrophenyl) disulfide. Because the disulfide is insoluble in carbon tetrachloride, the sulfenyl bromide may be readily purified by recrystallization; yield 75–80%, m.p. 102–104°.

3. Discussion

2,4-Dinitrophenyl benzyl sulfide has been prepared by the reaction of benzyl chloride with 2,4-dinitrothiophenol[2] or *bis*-(2,4-dinitrophenyl) disulfide[3] and by the condensation of 2,4-dinitrochlorobenzene with benzyl mercaptan.[4]

2,4-Dinitrobenzenesulfenyl chloride has been obtained by the chlorinolysis of 2,4-dinitrophenyl thiolbenzoate,[5] 2,4-dinitrothiophenol,[6] or *bis*-(2,4-dinitrophenyl) disulfide,[7,8] and by the present procedure.[9]

4. Merits of the Preparation

2,4-Dinitrobenzenesulfenyl chloride is a versatile analytical reagent for the characterization of a wide variety of organic compounds, including alcohols, mercaptans, ketones, olefins, amines, aromatic compounds, olefin oxides, and hydroxysteroids. Review articles summarize these applications.[10,11]

The chlorinolysis of 2,4-dinitrophenyl benzyl sulfide gives a good yield of product which is satisfactory for most purposes without recrystallization. Only simple equipment and inexpensive materials are needed, only 2 or 3 hours of the operator's time are required, and the entire procedure can be completed within 24 hours.

The best previous method of preparation, the chlorinolysis of *bis*-(2,4-dinitrophenyl) disulfide by sulfuryl chloride in the presence of pyridine,[8] requires much more time and effort with results that are uncertain, even for experienced operators.

References and Notes

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

petroleum ether

sulfenyl chloride

sulfenyl bromide

methanol (67-56-1)

bromine (7726-95-6)

carbon tetrachloride (56-23-5)

ethylene chloride (107-06-2)

sulfuryl chloride (7791-25-5)

pyridine (110-86-1)

benzyl chloride (100-44-7)

2,4-dinitrochlorobenzene (97-00-7)

2,4-Dinitrobenzenesulfenyl chloride,
Benzenesulfenyl chloride, 2,4-dinitro- (528-76-7)

benzyl mercaptan (100-53-8)

2,4-Dinitrophenyl benzyl sulfide (7343-61-5)

2,4-Dinitrobenzenesulfenyl bromide

2,4-dinitrothiophenol

2,4-dinitrophenyl thiolbenzoate

bis-(2,4-dinitrophenyl) disulfide (2217-55-2)