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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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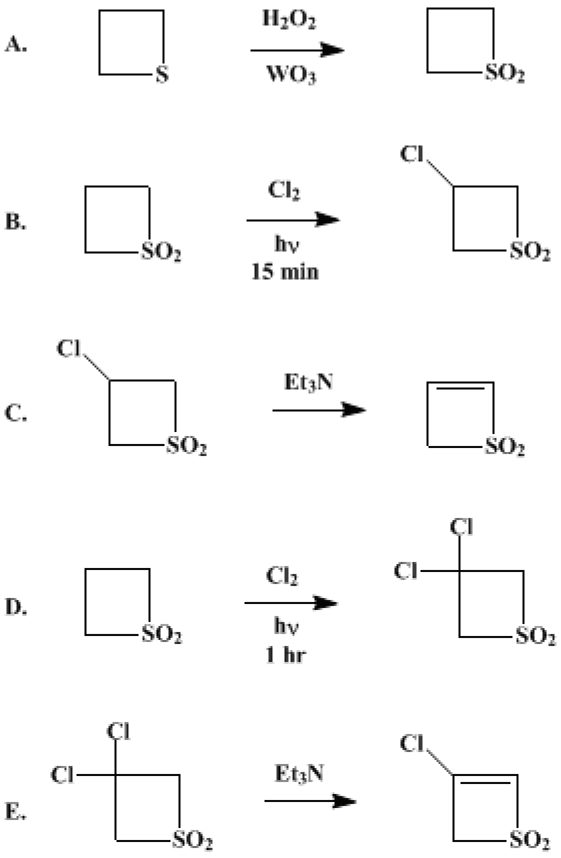
THIETE 1,1-DIOXIDE AND 3-CHLOROTHIETE 1,1-DIOXIDE

[2*H*-Thiete 1,1-dioxide and 2*H*-thiete, 3-chloro- 1,1-dioxide]



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1. Procedure

A. *Thietane 1,1-dioxide.* The pH of a solution of tungstic acid ($WO_3 \cdot H_2O$) (1.1 g, 0.044 mol) (Note 1) in 280 mL of distilled water is adjusted to 11.5 by addition of 10% aqueous sodium hydroxide; the white suspension of the tungstate catalyst is added to a 1-L, round-bottomed flask fitted with a mechanical stirrer and a pressure-equalizing addition funnel. The tungstic acid–water mixture is cooled to 0–10°C by means of an ice–salt bath; glacial acetic acid (50 mL) and trimethylene sulfide (thietane) (47.5 g, 0.641 mol, *d* 1.028) (Note 2) are added. The chilled mixture is stirred, and 30% hydrogen peroxide (189 mL) is added carefully by means of the addition funnel over a period of 2 hr (Note 3). The mixture is stirred at 0–10°C for an additional hour, transferred to an evaporating dish, and heated to near dryness on a steam bath. The resulting solid material is triturated five times with 100-mL portions of hot chloroform; any catalyst is removed by filtration. The chloroform solutions are combined and dried over anhydrous magnesium sulfate and the solvent is removed via a rotary evaporator to give a white solid (60.3–63.7 g, 0.57–0.60 mol, 88.7–93.7%), mp 74–76°C (lit.[2] mp 75.5–76°C).

B. *3-Chlorothietane 1,1-dioxide.* Thietane 1,1-dioxide (14.0 g, 0.132 mol) is placed in a three-necked, 500-mL, round-bottomed flask fitted with a magnetic stirrer, reflux condenser and a chlorine bubbler. *Caution! (Since chlorine is poisonous, the reaction involving it should be done in a good hood.)* Carbon tetrachloride (300 mL) is added to the flask (Note 4) and the suspension is irradiated by a 250-W sunlamp positioned as close as possible to the reaction flask without touching it (Note 5) while chlorine is bubbled through the solution for 15 min at a moderate rate (Note 6). A copious white precipitate forms and irradiation and addition of chlorine must be stopped at this point (or 10 min after the first appearance of a precipitate) to avoid dichlorination. The reaction mixture is cooled to room temperature and filtered to give a white, fluffy product (5.4–8.1 g, 30–44%) that is crystallized from chloroform, mp 136–137°C (lit.[3] mp 136.5–137.5°C).

C. *Thiete 1,1-dioxide.* A sample of 3-chlorothietane 1,1-dioxide (8.0 g, 0.057 mol) is dissolved in dry toluene (300 mL) (Note 7) in a 500-mL, two-necked, round-bottomed flask equipped with a reflux condenser, magnetic stirrer, heating mantle (or silicone oil bath), and thermometer. The reaction is heated to 60°C and triethylamine (28.7 g, 0.28 mol, 39.5 mL) is added through the condenser. The reaction mixture is stirred for 4 hr and triethylamine hydrochloride is removed by filtration and washed with toluene (100 mL). Toluene is removed on a rotary evaporator and the residue is recrystallized from diethyl ether–ethanol (Note 8) to give a white solid (4.5–4.8 g, 75–81%); mp 49–50°C (lit.[3] mp 52–54° C).

D. *3,3-Dichlorothietane 1,1-dioxide.* Thietane 1,1-dioxide (5.0 g, 0.047 mol) is placed in a 500-mL, three-necked, round-bottomed flask equipped with a reflux condenser, magnetic stirrer, and chlorine gas bubbler. Carbon tetrachloride (350 mL) is added and the solution is irradiated with a 250-W sunlamp (Note 5) while chlorine is bubbled through the stirred mixture for 1 hr (Note 9). Irradiation and chlorine addition are stopped and the reaction mixture is allowed to cool to room temperature. The product is collected by filtration as a white solid (4.0–4.4 g, 49–53%), mp 156–158°C[4] (Note 10). the product can be used without further purification or recrystallized from chloroform.

E. *3-Chlorothiete 1,1-dioxide.* A solution of 3,3-dichlorothietane 1,1-dioxide (4.0 g, 0.023 mol) in toluene (150 mL) is placed in a 250-mL, round-bottomed, two-necked flask equipped with a heating mantle (or silicone oil bath), magnetic stirrer, reflux condenser, and thermometer. The solution is heated to 60°C and triethylamine (2.54 g, 0.025 mol, 3.5 mL) is added dropwise through the condenser over a 10-min period. The solution is stirred for 2 hr at 60°C and cooled to room temperature. The triethylamine hydrochloride is collected by filtration and washed with hot toluene (50 mL). Removal of toluene on a rotary evaporator gives a white solid (2.7–3.0 g, 84–93%) that is recrystallized from chloroform-hexane, mp 118–120°C[4] (Note 11).

2. Notes

1. The tungstic acid was used as supplied by the Eastman Kodak Company.
2. The trimethylene sulfide was used as supplied by the Aldrich Chemical Company.
3. The addition rate of the hydrogen peroxide must be adjusted so that the temperature of the reaction mixture does not rise above 10°C. The yield is reduced if the temperature is allowed to rise above that point. The endpoint of the reaction, when excess peroxide is present, can be determined with potassium iodide–starch test paper. The yield also is reduced if more than a slight excess of hydrogen peroxide is used.
4. The sulfone is not completely dissolved at this point. The prescribed ratio of sulfone to carbon tetrachloride (0.0467 g mL) is important. If it is less (i.e., more carbon tetrachloride relative to sulfone), considerable 3,3-dichlorothietane 1,1-dioxide will be formed.
5. Any commercial sunlamp is satisfactory and should be used with eye protection. Carbon tetrachloride boils gently because of the heat from the lamp.
6. The submitters suggested adding the chlorine at such a rate that a constant yellow color is maintained in the solution or suspension. The checkers found that, depending on the rate of chlorine introduction, it took from 10 to 35 min for the appearance of the white precipitate. In each run, the monochlorinated product was contaminated with a small amount (5–10% by NMR integration) of either starting material or dichlorinated product. The checkers found that the optimum yield of monochlorinated product was obtained when the chlorine was bubbled into the solution through a ¼-in. glass tube at a rate estimated to be between 5–15 bubbles per second. The suspended sulfone dissolves as the reaction proceeds.
7. Toluene was dried over Linde 4A molecular sieves. Benzene may be used also.
8. The product is heated in about 25–30 mL of diethyl ether, and ethanol is added dropwise until a solution is obtained. The checkers found that the thiete sulfone could also be crystallized by gently heating the crude material in diethyl ether (~ 100 mL) until it dissolves, followed by cooling to −15°C.

9. If the reaction time is less than 1 hr, a mixture of monochloro- and dichlorosulfone is obtained.
10. The spectral properties of the product are as follows: IR (KBr disk) cm^{-1}: 2950 (m), 1370 (m, SO_2), 1310 (m), 1210 (m), 1140 (m, SO_2), 970 (m), 940 (m), 820 (w); ^{1}H NMR (chloroform-*d*) δ: 5.0 (s, 4 H, $CH_2SO_2CH_2$).
11. The spectral properties of the product are as follows: IR (KBr disk) cm^{-1}: 1540 (m, >C=C<), 1400 (w), 1300 (s, SO_2), 1210 (s), 1140 (s, SO_2), 1020 (m), 770 (m); ^{1}H NMR (chloroform-*d*) δ: 4.6 (s, 2 H, CH_2-SO_2), 6.8 (s, 1 H, CH=C).

3. Discussion

This preparation of thiete 1,1-dioxide is more direct and less tedious than previous methods.[3,5,6]

Oxidation of trimethylene sulfide catalyzed by tungstic acid[7] is preferred to the uncatalyzed reaction; yields are better and the reaction time is shortened by elimination of an induction period.

Selective chlorination of the 3-position of thietane 1,1-dioxide may be a consequence of hydrogen atom abstraction by a chlorine atom. Such reactions of chlorine atoms are believed to be influenced by polar effects, with preferential hydrogen abstraction occurring remotely from an electron withdrawing group.[8] The free-radical chain reaction may be propagated by attack of the 3-thietanyl 1,1-dioxide radical on molecular chlorine.

Conversion of 3-chlorothietane 1,1-dioxide to the 3-(*N,N*-dimethylamino) derivative followed by reduction, quaternization, and Hofmann elimination affords a convenient route to the highly reactive thiete (thiacyclobutene).[5,9]

The following compounds have been obtained from thiete 1,1-dioxide: substituted cycloheptatrienes,[10] benzyl α-toluenethiosulfinate,[11] pyrazoles,[12] naphthothiete 1,1-dioxides,[13] and 3-substituted thietane 1,1-dioxides.[14] It is a dienophile in Diels–Alder reactions[10,13,15] and undergoes cycloadditions with enamines, dienamines, and ynamines.[16] Thiete 1,1-dioxide is a source of the novel intermediate, vinylsulfene (CH_2=CHCH=SO_2), which undergoes cycloadditions to strained olefinic double bonds,[17] reacts with phenol to give allyl sulfonate derivatives[18] or cyclizes unimolecularly to give an unsaturated sultene.[18] Platinum[19] and iron[20] complexes of thiete 1,1-dioxide have been reported.

3-Chlorothiete 1,1-dioxide is a useful intermediate for the preparation of other 3-substituted thiete 1,1-dioxides via addition–elimination reactions.[4] It also undergoes Diels–Alder reactions with 1,3-butadiene and with 1,3-diphenylisobenzofuran.[4]

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

H_2O

monochloro- and dichlorosulfone

thiete (thiacyclobutene)

ethanol (64-17-5)

acetic acid (64-19-7)

Benzene (71-43-2)

diethyl ether (60-29-7)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

chloroform (67-66-3)

iron (7439-89-6)

phenol (108-95-2)

carbon tetrachloride (56-23-5)

platinum (7440-06-4)

chlorine (7782-50-5)

toluene (108-88-3)

hydrogen peroxide,
peroxide (7722-84-1)

Triethylamine hydrochloride (554-68-7)

magnesium sulfate (7487-88-9)

1,3-Butadiene (106-99-0)

triethylamine (121-44-8)

benzyl α-toluenethiosulfinate

allyl sulfonate

1,3-diphenylisobenzofuran (5471-63-6)

chloroform-hexane

Thiete 1,1-dioxide,
2H-Thiete 1,1-dioxide (7285-32-7)

3-Chlorothiete 1,1-dioxide,
2H-thiete, 3-chloro- 1,1-dioxide (90344-86-8)

tungstic acid

trimethylene sulfide,
thietane (287-27-4)

Thietane 1,1-dioxide (5687-92-3)

3-Chlorothietane 1,1-dioxide (15953-83-0)

3,3-Dichlorothietane 1,1-dioxide (90344-85-7)