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## PREPARATION OF DIALKYL DISULFIDES

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This invention relates to new and useful improvements  
in processes for the preparation of dialkyl disulfides,  
and more particularly to the preparation of dialkyl disulfides  
by partial oxidation of primary and secondary mercap-  
tans with nitrogen dioxide.

The chemistry of organic sulfur compounds has been  
investigated extensively in recent years as a result of the  
necessity for removing sulfur compounds from petroleum  
fractions. Mercaptans occur extensively in petroleum  
or are produced in the refining of petroleum fractions,  
and the utilization of these compounds is important if  
maximum return is to be obtained for petroleum prod-  
ucts. Alkyl sulfides and disulfides are well-known or-  
ganic sulfur compounds which have a variety of uses.  
These compounds are intermediate in the formation of  
other sulfur-containing organic compounds and in some  
cases are useful as solvents. Mercaptans have been oxi-  
dized to dialkyl disulfides by a variety of oxidizing  
agents, see "Organic Chemistry of Bivalent Sulfur," Reid,  
Chemical Publishing Company, 1958. Mercaptans have  
been oxidized by air or oxygen in the presence of aqueous  
alkali. Mercaptans have also been oxidized by ozone,  
permanganates, perborates, fuming nitric acid, chlorine,  
iodine, etc. The various techniques of oxidation of mer-  
captans with the oxidation agents reported in the prior  
art give rise to a variety of products. In some cases  
monosulfides are formed, while in other cases disulfides  
or polysulfides are formed. In many cases the sulfides  
which are formed in the oxidation process are further  
oxidized to sulfones, sulfoxides, and sulfonic acids.

It is therefore one object of this invention to provide  
a new and improved process for the preparation of di-  
alkyl disulfides and alkyl thionitrites in good yield and  
high selectivity.

A feature of this invention is the provision of an im-  
proved process for the preparation of dialkyl disulfides  
and alkyl thionitrites by reaction of nitrogen dioxide with  
a primary or secondary aliphatic mercaptan. Another  
feature of this invention is the provision of an improved  
process for the preparation of dialkyl disulfides and alkyl  
thionitrites in which a primary or secondary  $C_1$ - $C_{16}$  alkyl  
mercaptan is reacted with nitrogen dioxide at a tempera-  
ture of about  $-50^\circ$  to  $+250^\circ$  C. under essentially  
anhydrous conditions.

Other objects and features of this invention will be-  
come apparent from time to time throughout the specifi-  
cation and claims as hereinafter related.

This invention is based upon our discovery that dialkyl  
disulfides can be produced in excellent yields, together  
with small amounts of alkyl thionitrites, by the uncata-  
lyzed reaction of primary or secondary alkyl mercaptans  
with nitrogen dioxide under essentially anhydrous condi-  
tions. The reaction is exothermic and takes place  
readily at room temperature although it may be carried  
out at ambient temperatures ranging from  $-50^\circ$  to  
 $+250^\circ$  C. In carrying out this process, a primary or  
secondary alkyl mercaptan (preferably a  $C_1$ - $C_{16}$  primary  
or secondary alkyl mercaptan) is contacted with nitro-  
gen dioxide in a reactor. The reaction can be carried  
out in any convenient reaction system, and the reactor  
may be of any material of construction which is inert  
toward the reactants and products of reaction under re-  
action conditions. The reactor may be made of glass,

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quartz, stainless steel, etc. When the mercaptan is  
mixed with nitrogen dioxide, an instantaneous exothermic  
reaction takes place which completely consumes the  
nitrogen dioxide (unless an excess of nitrogen dioxide is  
used). When a lower mercaptan (e.g.,  $CH_3SH$ ,  
 $C_2H_5SH$ ,  $C_3H_7SH$ ) is reacted, the reaction is preferably  
carried out in the gas phase. When a higher boiling  
mercaptan is reacted, the nitrogen dioxide is bubbled  
through (or otherwise contacted with) the liquid mer-  
captan. The ratio of reactants in the gas-phase reaction  
is not critical and the mercaptan and nitrogen dioxide  
may be fed in widely varying mol ratios ranging from  
1:10 to 20:1. When the reaction is carried out in liquid  
phase, it is preferred to avoid the use of a stoichiometric  
excess of nitrogen dioxide as the results in the formation  
of sulfoxides or sulfones rather than the desired disul-  
fides. The rate of feed of reactants is not critical and  
the total gaseous hourly space velocity of reactants in the  
gas-phase reaction may vary widely from as little as 50  
to as high as 5000 or more. Equivalent feed rates can  
be used in the liquid-phase reaction. The reaction prod-  
ucts are withdrawn from the reaction zone, and settle  
into two phases. The lower phase consists essentially of  
water and some dissolved products. The upper phase,  
which is bright red, consists essentially of a dialkyl di-  
sulfide (derived from the mercaptan) containing in solu-  
tion a small amount of an alkyl thionitrite. When the  
upper phase is separated, dried, and heated, the thio-  
nitrite is decomposed and a substantially pure dialkyl di-  
sulfide is obtained as the product. This process is lim-  
ited to the reaction of nitrogen dioxide with primary and  
secondary alkyl mercaptans under essentially anhydrous  
conditions (i.e., free of water other than the byproduct  
water of reaction). Mercaptans which may be used in  
this reaction include methanethiol, ethanethiol, propane-  
thiol (both primary and secondary isomers), pentane-  
thiol, hexanethiol, octanethiol, decanethiol, dodecane-  
thiol, hexadecanethiol, etc.

The following non-limiting examples are illustrative of  
the scope of this invention.

## EXAMPLE I

A 21-mm. O.D. glass reactor-tube, having a volume  
of 92 cc., was mounted vertically and connected so that  
two separate gas streams could be charged at the top.  
Helium at 60 cc./min. was bubbled through ethanethiol  
at room temperature and charged to the reactor tube at  
an ethanethiol flow rate of 46 cc./min. Nitrogen dioxide  
was also charged at the top of the reactor tube at  
a rate of 39 cc./min. At the point in the reactor tube  
where the two gas streams met, there was an exothermic  
reaction with the formation of a liquid product.

The gaseous and liquid products of the reaction were  
withdrawn from the bottom of the reactor over a cold-  
finger condenser and into a large glass receiver. From  
this point, gaseous products were directed through a con-  
denser and then a gas-sampling tube. The final gaseous  
product was essentially colorless, thus indicating that  
most of the nitrogen dioxide had been consumed in the  
reaction. After a run of 45 minutes duration, there was  
obtained 6.6 ml. of a liquid product which had separated  
into two phases. The lower phase (0.7 ml.) was almost  
colorless while the upper phase (5.9 ml.) was cherry-red.

The lower liquid phase was separated and analyzed by  
infrared spectroscopy. This phase was found to consist  
essentially of water. The upper phase was analyzed by  
infrared spectroscopy and found to consist of about 65%  
diethyl disulfide, together with a small amount of diethyl  
sulfide. The intense red color was an indication of the  
formation of ethyl thionitrite (there is no accurate meth-  
od of analysis for thionitrites). Mass spectrometric  
analyses of the charge and product gas samples showed

that nitric oxide was a major gaseous product while a minor amount of sulfur dioxide was formed.

In this run, ethanethiol and nitrogen dioxide were fed in a mol ratio of 1.18 mols of the former to 1 mol of the latter. In the reaction, 91.2% of the ethanethiol was consumed and diethyl disulfide was formed in a yield of 73.4% (based on ethanethiol charged) and a selectivity of 80.5% (based on ethanethiol consumed in the reaction). In this reaction there was also produced a small amount of dimethyl disulfide which resulted from a small amount (6.5%) of methanethiol in the feed.

#### EXAMPLE II

The apparatus described in Example I is used for carrying out the reaction of methanethiol with nitrogen dioxide. Helium diluent at 50 cc./min. and methanethiol gas at 110 cc./min. are charged to the top of the reactor tube. Nitrogen dioxide gas at 50 cc./min. is also charged to the top of the reactor tube. At the point in the tube where the gas streams mix, there is an exothermic reaction with the formation of a liquid product. The liquid product is separated as in Example I and an aqueous phase is separated and discarded. The non-aqueous phase consists of a major amount of dimethyl disulfide and a minor amount of methyl thionitrite, together with small amounts of dimethyl sulfide. In this reaction, dimethyl disulfide can be produced in yields in excess of 70% and selectivities approaching 100%.

#### EXAMPLE III

An apparatus similar to that used in Example I is used for the reaction of various mercaptans with nitrogen dioxide under the conditions set forth in Table I and with the results indicated therein. The only change in procedure is that the mercaptans are charged to the reactor tube as liquids.

Table I

Mercaptan	Mercaptan: NO <sub>2</sub> Ratio	Reaction Temp., ° C.	Products
CH <sub>3</sub> CHCH <sub>3</sub> ----- SH	2.5	70	CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH-S-S-CH-CHSNO CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub>
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> SH-----	2.5	110	n-C <sub>4</sub> H <sub>9</sub> -S-S-n-C <sub>4</sub> H <sub>9</sub> +nC <sub>4</sub> H <sub>9</sub> SNO
CH <sub>3</sub> CHCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ----- SH	2.5	130	CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH-S-S-CH-CHSNO C <sub>2</sub> H <sub>5</sub> C <sub>2</sub> H <sub>5</sub> CH <sub>3</sub> H <sub>7</sub>
nC <sub>8</sub> H <sub>17</sub> SH-----	2.5	220	nC <sub>8</sub> H <sub>17</sub> -S-S-nC <sub>8</sub> H <sub>17</sub> +nC <sub>8</sub> H <sub>17</sub> SNO

#### EXAMPLE IV

A glass flask was charged with 32.7 g. liquid ethanethiol and a mixture of helium and nitrogen dioxide was bubbled therethrough at 30 cc./min. each for 110 minutes. The total amount of nitrogen dioxide charged provided a mercaptan/nitrogen dioxide mol ratio of 3.1:1. On contact with the nitrogen dioxide, the ethanethiol reddened and the color progressively deepened. The red color is attributed to the formation of ethyl thionitrite (which is deep red in color), but no analytical procedure for identification of thionitrites is available. The gaseous effluent from the flask was colorless, thus indicating that no unreacted nitrogen dioxide was present. The final liquid product consisted of two phases, a deep cherry red upper phase and a small amount of a clear, colorless lower phase (mostly water). Analysis of the product gas by mass spectrometer showed that it contained helium, nitric oxide, ethanethiol, and water. Distillation and an infrared analysis of the red liquid showed that diethyl

disulfide and unreacted ethanethiol were the major components. In this experiment about 54% of the mercaptan was consumed. Diethyl disulfide was obtained in a yield of about 30% based on the nitrogen dioxide charged to the reaction.

#### EXAMPLE V

A gas flask, equipped with a stirrer and bubbler tube, was charged with 150 g. n-dodecanethiol (0.741 mol) and 200 ml. carbon tetrachloride. Gaseous nitrogen dioxide (40 cc./min.) and nitrogen (20 cc./min.) were bubbled into the stirred liquid mixture until 6.7 g. (0.146 mol) nitrogen dioxide were charged. The temperature of the reaction mixture was maintained at 24° C. during the reaction. In this experiment di-dodecyl disulfide was obtained with the yield of 84.2% based on the nitrogen dioxide (limiting reactant) charged.

When the same reaction was carried out using water as the diluent for the reaction, the yield of the product disulfide was less than half obtained using a non-aqueous solvent.

From the foregoing examples and other experimental work, we have found that good yields of dialkyl disulfides and alkyl thionitrites can be obtained by the reaction of nitrogen dioxide with one or more primary or secondary alkanethiols at ambient temperatures. Where low-molecular-weight mercaptans are used as the reactant, the reaction is preferably carried out in gas phase, although a liquid-phase reaction in an inert solvent (such as carbon tetrachloride, hydrocarbons, etc.) can be used. The reaction is carried out at temperatures in the range of about -50° to +250° C. at a mercaptan/nitrogen dioxide mol ratio in the range of about 1:10 to 20:1. The reaction is preferably carried out at temperatures of about 0°-30° C. In the gas-phase reaction, the reaction can be carried out using a wide range of reactant ratios. In the liquid-phase reaction an excess of nitrogen diox-

ide should be avoided since it tends to reduce the yield of disulfides by forming solid reaction products. In the liquid-phase reaction, the use of an inert solvent is preferred and the reaction should be carried out under substantially anhydrous conditions (i.e., in the absence of water other than the by-product water of reaction). The reaction is limited to primary and secondary mercaptans since the reactions of tertiary mercaptans with nitrogen dioxide usually produces alkyl thionitrites.

While we have described our invention fully and completely with special emphasis on several preferred embodiments thereof, we wish it to be understood that within the scope of the appended claims this invention may be practiced otherwise than as specifically described herein.

The embodiments of the invention in which an exclusive property or privilege is claimed are as follows:

1. A method of preparing dialkyl disulfides and alkyl thionitrites which comprises reacting nitrogen dioxide

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under anhydrous conditions with at least one alkyl mercaptan selected from the group consisting of primary and secondary mercaptans, at a mercaptan/nitrogen dioxide mol ratio in the range of about 1:10 to 20:1 with the provision that a stoichiometric excess of said mercaptan is used when the reaction is carried out in liquid phase, and a reaction temperature of about  $-50^{\circ}$  to  $+250^{\circ}$  C.

2. A method in accordance with claim 1 in which the mercaptan reactant is methanethiol and the product is a mixture of dimethyl disulfide and methyl thionitrite.

3. A method in accordance with claim 1 in which the mercaptan reactant is ethanethiol and the product is a mixture of diethyl disulfide and ethyl thionitrite.

4. A method in accordance with claim 1 in which methanethiol and nitrogen dioxide are mixed at room temperature to effect a spontaneous exothermic reaction and a liquid product is obtained consisting essentially of a mixture of dimethyl disulfide and methyl thionitrite.

5. A method in accordance with claim 1 in which ethanethiol and nitrogen dioxide are mixed at room temperature to effect a spontaneous exothermic reaction and a liquid product is obtained consisting essentially of a mixture of diethyl disulfide and ethyl thionitrite.

6. A method in accordance with claim 1 in which the reaction is carried out in an inert non-aqueous diluent.

7. A method in accordance with claim 6 in which nitrogen dioxide is bubbled into a mixture of n-dodecanethiol and carbon tetrachloride to produce di-n-dodecyl disulfide.

8. A method in accordance with claim 1 in which the reaction is carried out at a temperature of about  $0^{\circ}$ – $30^{\circ}$  C.

9. A method for the partial oxidation of mercaptans which comprises reacting nitrogen dioxide under anhy-

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drous conditions with at least one alkyl mercaptan selected from the group consisting of primary and secondary mercaptans, at a temperature of about  $-50^{\circ}$  to  $+250^{\circ}$  C., said reaction being carried out in liquid phase using a stoichiometric excess of said mercaptan, and recovering an organic product containing a major portion of a dialkyl disulfide.

10. A method for the partial oxidation of mercaptans which comprises reacting nitrogen dioxide under anhydrous conditions with at least one lower alkyl mercaptan selected from the group consisting of primary and secondary mercaptans, at a temperature of about  $-50^{\circ}$  to  $+250^{\circ}$  C., said reaction being carried out in gas phase at a total gaseous hourly space velocity of reactants in the range from about 50 to 5,000, and recovering an organic product containing a major portion of a dialkyl disulfide.

11. A method of preparing dialkyl disulfides and alkyl thionitrites which comprise reacting nitrogen dioxide under anhydrous conditions with at least one lower alkyl mercaptan selected from the group consisting of primary and secondary mercaptans, said reaction being carried out in gas phase at a mercaptan/nitrogen dioxide mol ratio in the range of about 1:10 to 20:1 and at a temperature of about  $-50^{\circ}$  to  $+250^{\circ}$  C.

12. A method in accordance with claim 11 in which the total gaseous hourly space velocity of reactants is in the range from about 50 to 5000.

#### References Cited in the file of this patent

##### UNITED STATES PATENTS

1,908,935	Tschunkur et al. .... May 16, 1933
2,307,624	George ..... Jan. 5, 1943
2,328,709	Crandall et al. .... Sept. 7, 1943

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,134,798

May 26, 1964

William L. Fierce et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 10, for "raio" read -- ratio --; line 15 for "the", first occurrence, read -- this --; column 5, line 33, for "whihc" read -- which --; column 6, line 9, for "dixoxide" read -- dioxide --.

Signed and sealed this 27th day of October 1964.

(SEAL)

Attest:

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UNITED STATES PATENT OFFICE  
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