

# PATENT SPECIFICATION

(11) 1 554 154

1 554 154

- (21) Application No. 3663/79 (22) Filed 15 May 1975  
 (62) Divided out of No. 1554153  
 (23) Complete Specification filed 14 May 1976  
 (44) Complete Specification published 17 Oct. 1979  
 (51) INT CL<sup>2</sup> C07C 149/14  
 (52) Index at acceptance  
 C2C 200 20Y 30Y 332 373 37Y 397 RV  
 (72) Inventor GEORGE RAYMOND WHITE

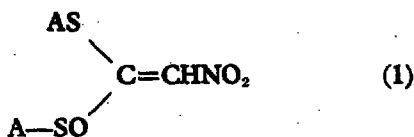


## (54) 2-LOWER ALKYL SULPHINYL-2-LOWER ALKYLTHIO-1-NITROETHYLENES

(71) We, SMITH KLINE & FRENCH LABORATORIES LIMITED, Mundells, Welwyn Garden City, Hertfordshire, England, a British company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the preparation of 2 - loweralkylsulphanyl - 2 - loweralkylthio - 1 - nitroethylenes which are useful for preparing 2 - amino - 2 - loweralkylthio - 1 - nitroethylene derivatives.

According to the invention we provide compounds of Structure 1



in which A is lower alkyl. Preferably A is methyl.

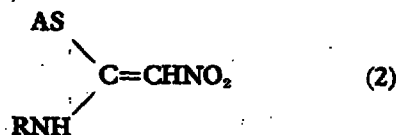
Throughout the present specification by the term 'lower alkyl' is meant an alkyl group containing 1 to 4 carbon atoms.

The compounds of Structure 1 can be prepared by reacting a compound (AS)<sub>2</sub>C=CHNO<sub>2</sub> with an oxidising agent, for example hydrogen peroxide. This reaction can be carried out in a solvent, for example acetic acid. Preferably one equivalent of hydrogen peroxide (i.e. sufficient to oxidise one lower alkylthio group) is used as the oxidising agent. Preferably when hydrogen peroxide is used as the oxidising agent and when the reaction is carried out in acetic acid the reaction is carried out at 60°C.

The compounds of Structure 1 can exist as two geometrical isomers, i.e. in the 'Z' and in the 'E' form, and the two isomers of the compound of Structure 1 in which A is methyl can be separated by fractional crystallisation.

The compounds of Structure 1 can be converted into 2 - amino - 2 - alkylthio - 1 - nitroethylene derivatives by reaction with an

amine as described in our co-pending application 20628/75 (Serial No. 1,554,153). These derivatives are useful intermediates for preparing 2,2 - diamino - 1 - nitroethylene compounds, for example the compounds described as having histamine H<sub>2</sub>-antagonist activity in British Patent Specification No. 1,421,792. When the compounds of Structure 1 are reacted with an equivalent amount of an amine RNH<sub>2</sub>, the compound of Structure 2



is produced without the formation of significant amounts of the bis compound (RNH)<sub>2</sub>C=CHNO<sub>2</sub>.

The invention is illustrated but in no way limited by the following Example:—

### EXAMPLE

1 - Methylsulphanyl - 1 - methylthio - 2 - nitroethylene

To a stirred solution in acetic acid (4,500 ml) of 1,1 - bis - methylthio - 2 - nitroethylene (165 g) at 60° was added over 15 minutes 30% (100 volume) hydrogen peroxide (113 ml) and the reaction mixture maintained, with stirring, at 60° for 17 hours. Evaporation of the solvent under reduced pressure gave a residue which was taken up in methylethylketone, re-evaporated and finally crystallised from methylethylketone to yield the title product as a yellow solid m.p. 137—143°. Further purification yielded the pure "Z" and "E" isomers. One of these had m.p. 145—148° and from the mother liquors the other isomer was obtained after further working up and recrystallisation from methylal had m.p. 90—93°.

Found:

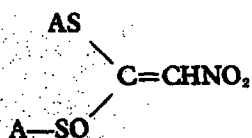
C, 26.7; H, 3.9; N, 7.7; S, 35.1%  
 C<sub>4</sub>H<sub>7</sub>NO<sub>2</sub>S<sub>2</sub>

requires:

C, 26.5; H, 3.9; N, 7.7; S, 35.4%

**WHAT WE CLAIM IS:—**

1. A compound of structure



in which A is lower alkyl.

5 2. 1 - Methylsulphanyl - 1 - methylthio - 2 - nitroethylene.

3. A compound of Claim 1 or Claim 2 in the form of a substantially pure geometric isomer.

10 4. A process for preparing a compound of any one of Claims 1 to 3 which comprises reacting a compound  $(\text{AS})_2\text{C}=\text{CHNO}_2$  with an oxidising agent.

5. A process according to Claim 4 in which the oxidising agent is hydrogen peroxide.

6. A process according to Claim 4 or Claim 5 in which the reaction is carried out in acetic acid.

7. A process according to Claim 5 or Claim 6 in which one equivalent of hydrogen peroxide is used.

8. A process according to Claim 7 which is carried out at 60°.

9. A process for preparing a compound of Claim 1 or Claim 2 substantially as herein-before described in the Example.

10. A compound of Claim 1 or Claim 2 whenever prepared by a process according to any one of Claims 4 to 9.

**G. H. HARGREAVES,**  
Chartered Patent Agent.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1979  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.



\* C L M S \*