

## Short Communications

### Reactions between Ketones and Ammonium Polysulphide

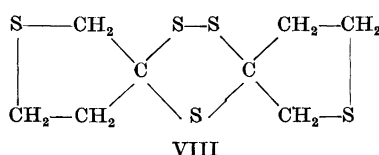
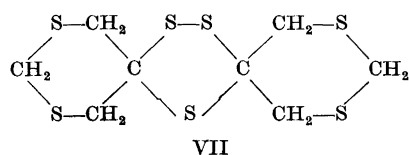
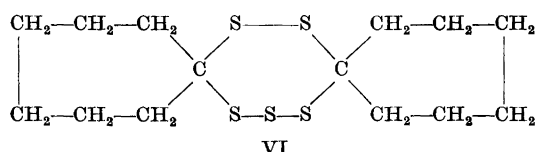
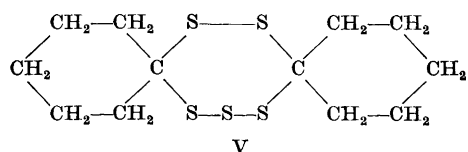
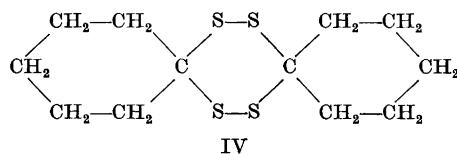
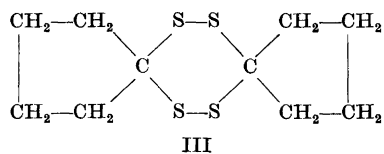
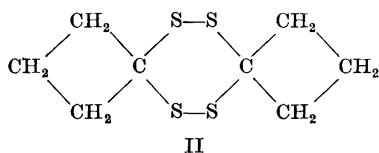
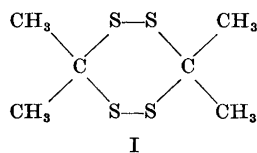
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Duplodithioacetone (I) and related compounds have been prepared by the reaction of a ketone and excess of aqueous ammonium polysulphide<sup>1,2</sup>. Asinger obtained 5- and 6-membered rings by allowing the carbonyl compound to react with elementary sulphur and an amine, saturated with hydrogen sulphide<sup>3,4</sup>. The author found

that duplodithioacetone was obtained without disturbing byproducts by running the reaction in alcohol-water solution at about +4°C for one to two days. As this is a way to avoid resinous material, attempts were made with other ketones under the same conditions.

With *cyclohexanone* white crystals were obtained, which were recrystallized from a mixture of chloroform and ethanol. However, the purified product was not the expected duplodithio*cyclohexanone* (IV) obtained by Fredga<sup>2</sup> but a compound with the composition of (V), bis-4,4,7,7-pentamethylene-1,2,3,5,6-pentathiepane. Such a pentathiepane (VI) was first obtained by Fredga from *cycloheptanone* and ammoniumpolysulphide<sup>2</sup>.



Cyclopentanone gives (III) after reaction in alcoholic or aqueous solution.

Cyclobutanone gives the compound (II) in aqueous solution<sup>5</sup>.

1,3-Dithian-5-on and 3-ketothiophane give five-membered rings (VII, VIII) of the type obtained by Asinger<sup>3,4</sup> in aqueous and alcohol-water solutions, respectively.

From the results it is apparent that the ring size is greatly dependent on the reaction conditions and the starting materials. More experiments to obtain 6-membered and larger rings are planned; results will be reported at a later date.

*Experimental.* Duplodithioacetone (3,3,6,6-tetramethyl-1,2,4,5-tetrathiane) (I). In a 300 ml Erlenmeyerflask 45 ml of acetone was mixed with 100 ml of ethanol and cooled to +4°C. A cooled solution of ammonium polysulphide (prepared by dissolving 20 g of ammonium-chloride in 77 ml of 2.5 M Na<sub>2</sub>S<sub>2</sub>) was added. The flask was closed, shaken for a minute and left in a refrigerator at about 0°C for 3 days. The crystals were then separated, washed with water to dissolve inorganic salts, dried and recrystallized 3 times from ethanol. In the first recrystallisation some Norit was added to remove colloidal sulphur. 6.57 g of duplodithioacetone with a m.p. of 94°–95° was found. On dilution of the motherliquor with water roughly 0.6 g of impure tetrathiane was obtained.

*Bis-4,4,7,7-pentamethylene-1,2,3,5,6-pentathiepane* (V). In a 200 ml Erlenmeyer flask 4 g of cyclohexanone was dissolved in 100 ml of ethanol and was allowed to react with ammonium disulphide as described above. The crude material (4.74 g) was recrystallised several times from chloroform and ethanol. Colourless flakes with m.p. 85°–87°C were obtained. The product is readily soluble in chloroform, carbontetrachloride and benzene. (Found: C 44.05, 44.29, 44.80; H 5.90, 6.53, 6.24; S 49.17, 49.20; Mol. wt: 316, 316. Calc. for C<sub>12</sub>H<sub>20</sub>S<sub>5</sub>: C 44.40; H 6.21; S 49.39; Mol. wt: 324.6).

The author is greatly indebted to Professor Arne Fredga for suggesting the present work, for stimulating discussions and for some starting materials. Thanks are further due to Dr. Göran Bergson and to Dr. Sven-Olov Lawesson for valuable advice during the preparation of this manuscript.

1. Willgerodt, C. *Ber.* **20** (1887) 2467.
2. Fredga, A. *Acta Chem. Scand.* **12** (1958) 891.
3. Asinger, F. *Angew. Chem.* **70** (1958) 372.
4. Asinger, F. *Angew. Chem.* **70** (1958) 667.
5. Fredga, A. *Private Communication.*

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## Mass Spectrometric Demonstration of Extensive Replacement of Hydrogen by Deuterium During Catalytic Deuteration of Methyl Oleate, Methyl 9,10-Dibromostearate, and Methyl 12-Chlorostearate

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In connection with work on the determination of the position of double bonds in unsaturated fatty esters by mass spectrometric analysis<sup>1</sup>, methyl stearate obtained by catalytic deuteration of methyl oleate over Adams' platinum catalyst at room temperature was submitted to analysis. The high-mass end of the mass spectrum reproduced in Fig. 1 shows clearly that deuterium has entered the chain not only in position 9,10. Instead of a single molecule-ion peak at  $m/e = 300$  and its isotope-peak, corresponding to the entrance of two deuterium atoms, we have a whole series of molecule-ion peaks, the intensities of which decrease in a regular manner with increasing mass number. It is evident from Fig. 1 that molecules of mass 330 have been present. In these molecules all hydrogen atoms except six have been replaced by deuterium. This extensive replacement is probably closely related to the double bond shifts which are known<sup>2</sup> to occur during catalytic hydrogenation of olefins. Exchange reactions with the saturated hydrocarbon chain seems excluded, as no deuterium could be detected in methyl stearate which had been submitted to the same treatment as methyl oleate above.

Attempted replacement of bromine by deuterium in methyl 9,10-dibromostearate, using Adams' platinum catalyst, failed until sodium carbonate was added, and then gave a debrominated ester with mass spectrum practically identical with that of the ester obtained by catalytic deuteration of methyl oleate. A reaction similar to the debromination of vicinal dibromides by zinc to give olefins<sup>3,4</sup> is probably involved.