

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).

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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.

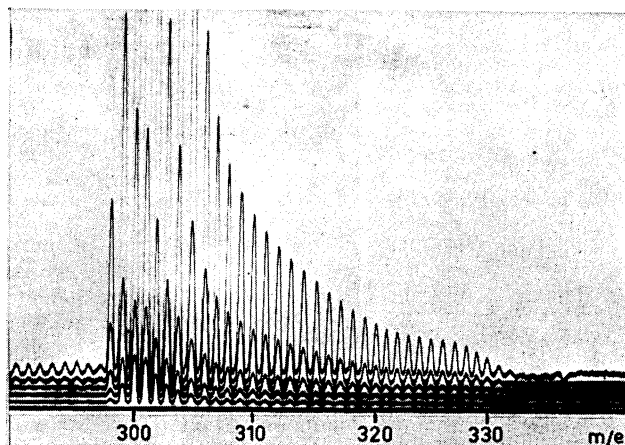


Fig. 1. High-mass end of mass spectrum of catalytically deuterated methyl oleate.

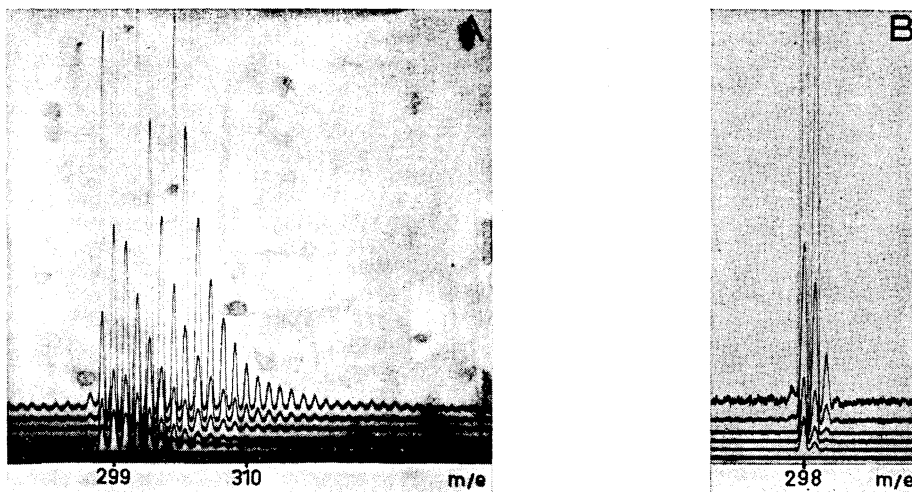


Fig. 2. A) High-mass end of mass spectrum of catalytically deuterated methyl 12-chlorostearate; B) High-mass end of mass spectrum of methyl stearate.

Deuteration of methyl 12-chlorostearate over Adams' platinum catalyst gave a dehalogenated ester without the use of sodium carbonate. The high-mass end of the mass spectrum of the ester is reproduced in Fig. 2A and shows that the molecule-ion peak at  $m/e = 299$ , corresponding to the replacement of chlorine by deute-

rium, is followed by about sixteen molecule-ion peaks of decreasing intensity. Molecules where deuterium have replaced nearly half the number of hydrogen atoms in the hydrocarbon chain have therefore been present.

Full details will be published later.

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## The Deswelling Action of Hydrazine on Nitrile Rubber

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In a previous paper<sup>1</sup> an outline was given of the primary and side reactions taking place when hydrazine or hydrazine hydrate reacts with linear homopolymers of acrylonitrile. Favourable conditions were found in homogeneous systems, as indicated by gel formation and disappearance of the strong infrared band at  $2\ 260\text{ cm}^{-1}$ , measuring the amount of nitrile groups in the sample. The primary polymer particle does not show this high degree of accessibility, but insolubilization occurs in both cases due to formation of interlinking units between macromolecules. The interlinking structural unit is 4-N-amino-1,2,4-triazole.

Such a reactivity is not found in copolymers of acrylonitrile and butadiene. Still more, *solubility* is limited already by the formation of microgel in the growing polymer particle at increasing degree of conversion during polymerization. Standard nitrile rubber latex with an acrylonitrile content of 37–40% dissolves in acetone, cyclohexanone or dioxane, yet with difficulty. The last mentioned solvent, however, shows a low solvent power, why phase separation instantly takes place when hydrazine is added (three phases!). Acetone and cyclohexanone are obviously unsuitable due to their reactivity.

A convenient way to study the action of an aqueous solution of hydrazine hydrate on the polymer is simply to add said reagent into a nitrile rubber latex with a low particle size. Commercial grades of butadiene-acrylonitrile latices are available for this purpose, e.g. Hycar Latex 1561, showing a medium particle size of 500 Å. The change of solubility characteristics can be observed at arbitrary intervals by casting a rubber film, preferably at reduced pressure or in a stream of dry nitrogen, followed by thorough washing in distilled water, soaking in acetone (if possible) and drying at 80°C in an inert atmosphere before use.

The weight swelling ratios of such a rubber film in a selected series of swelling agents is shown in Table 1. The degree of swelling is — rather arbitrarily — measured after an immersion time of 24 h in a large excess of liquid.

*Table 1.* Weight swelling ratios of nitrile rubber films, prepared at room temperature from a latex showing a solid content of 0.25 g.ml<sup>-1</sup>. Conc. of hydrazine hydrate: 0.85 g.ml<sup>-1</sup>. All samples preextracted in acetone at room temperature and dried at 80°C one hour before use. Time of reaction in the rubber latex: 24 h. Grade of nitrile rubber: High acrylonitrile content (37–40%), density in pure state 1.00, medium particle size 500 Å.

Swelling agent	Weight swelling ratio, g/g
Benzene	3.15
Toluene	2.82
Xylene (techn. grade)	2.25
Cyclohexane	1.10
Dipentene	1.52
Decalin	1.17
Chlorobenzene	6.77
Pyridine	8.42
Dioxane	4.92
Acetone	3.93
Cyclohexanone	8.08
2-Pyrrolidone	5.82
Dimethylformamide	7.61
Dimethylsulfoxide	4.73

A glance at the figures in Table 1 makes evident that the degree of swelling is qualitatively related to the molar volume of the solvent and its specific interaction coefficient with parent polymer. Such a