

On the Products Obtained from Ketones with Ammonium Polysulphide

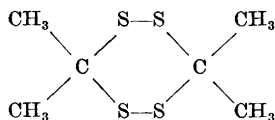
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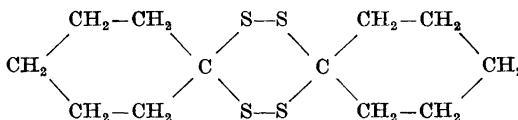
Two compounds obtained from *cyclohexanone* and *cycloheptanone* with ammonium polysulphide at room temperature are described (II, IV). The former contains a 1,2,4,5-tetrathiane ring in spirocyclic combination. The latter has a seven-membered ring with two carbon and five sulphur atoms (1,2,3,5,6-pentathiepane ring).

In 1887 Willgerodt published his first investigations on the reaction between ketones and ammonium polysulphide¹. At higher temperatures, the ketone is transformed to an amide; this rather peculiar reaction has been studied by several authors and is now generally known as Willgerodt's reaction².

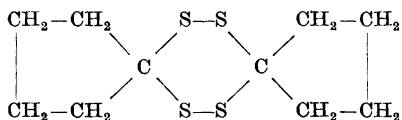
If a solution of polysulphide was left to stand with acetone at room temperature, however, Willgerodt obtained a crystalline compound answering to the formula $(\text{CH}_3)_2\text{CS}_2$. He assumed it to be dimeric and called it "duplo-dithioacetone". The structure was not discussed, but of course the formula I with a 1,2,4,5-tetrathiane ring is near at hand. In the "Ring Index" this structure is also postulated³. In connection with work in progress on the



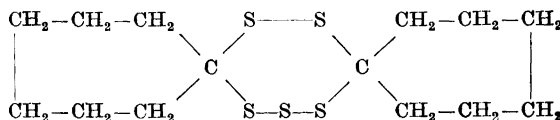
I



II



III



IV

disulphide group, an investigation on compounds of this type has been started in collaboration with Mr. B. Magnusson.

The acetone derivative is easily obtained according to Willgerodt's directions, but the preparation of higher homologues and derivatives from aromatic ketones met with difficulties, which have not been overcome as yet. Camphor did not react at all, even on standing for a long time. More promising results were obtained, however, with simple cyclic ketones. *Cyclohexanone* yields a readily crystallising compound (m.p. 130.5—131.5°), which must be ascribed the spirocyclic structure II. *Cyclopentanone* gives mostly dark-coloured, smeary products, but Mr. Magnusson could isolate the compound III (m.p. 151.5—153°) in low yield⁴.

The results obtained with *cycloheptanone* were rather unexpected. The compound isolated (m.p. 127—128°) has the formula $C_{14}H_{24}S_5$, thus containing five sulphur atoms instead of four. According to modern investigations^{5,6}, the occurrence of branched sulphur chains in organic compounds is very unlikely and the compound obtained from *cycloheptanone* must thus be ascribed the formula IV. To the author's knowledge, a ring containing two carbon and five sulphur atoms (1,2,3,5,6-pentathiepane) has not been described previously.

An explanation of the different behaviours of *cyclohexanone* and *cycloheptanone* cannot be given at present. Preliminary experiments with the two ketones and preparations of ammonium polysulphide with various amounts of sulphur (from $(NH_4)_2S_2$ to $(NH_4)_2S_4$) gave only the compounds II and IV, respectively, in some cases contaminated with free sulphur. It is possible that the crude reaction mixture represents a dynamic equilibrium of substances with different sulphur-containing rings (perhaps also open chain polymers), and that the most readily crystallising compound ultimately separates.

The question of the conformation of the sulphur-containing rings is of a certain interest. For the six-membered ring, the rigid chair form (Fig. 1 A) is of course possible. The corresponding boat form is pliable and permits a series of arrangements; two extreme forms are represented by Figs. 1 B and C. Owing to the rather bulky groups attached to the carbon atoms, formula B must be excluded, but the boat form C seems quite reasonable and must be taken into consideration. The formulas A and B are symmetrical (the former has also a center of symmetry) and the sulphur atoms lie in one plane. Formula C has no plane or center of symmetry and the sulphur atoms are not situated in the same plane.

A crystallographic investigation has been started by Dr. I. Lindqvist in collaboration with Mr. R. Rosenstein, who have kindly submitted some preliminary results. As stated already by Willgerodt, the acetone derivative (I)

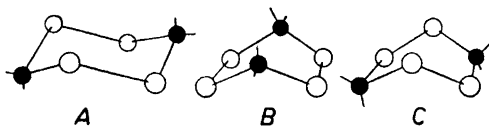


Fig. 1. Conformations of the tetra-thiane ring.

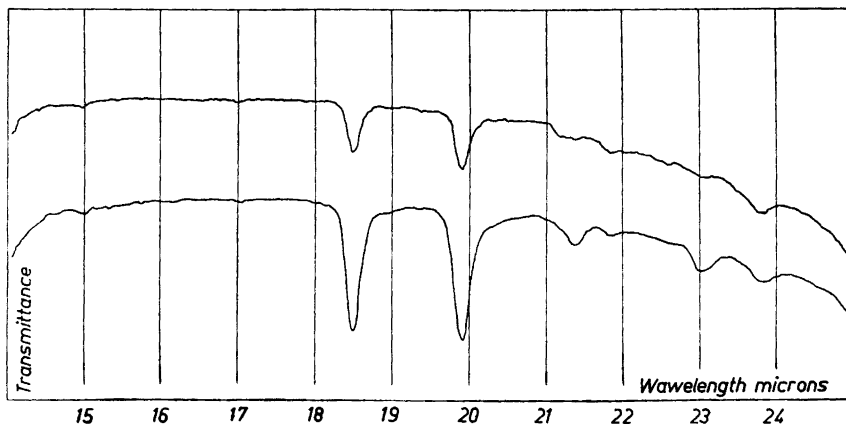


Fig. 2. IR absorption curve of the *cyclohexanone* derivative.

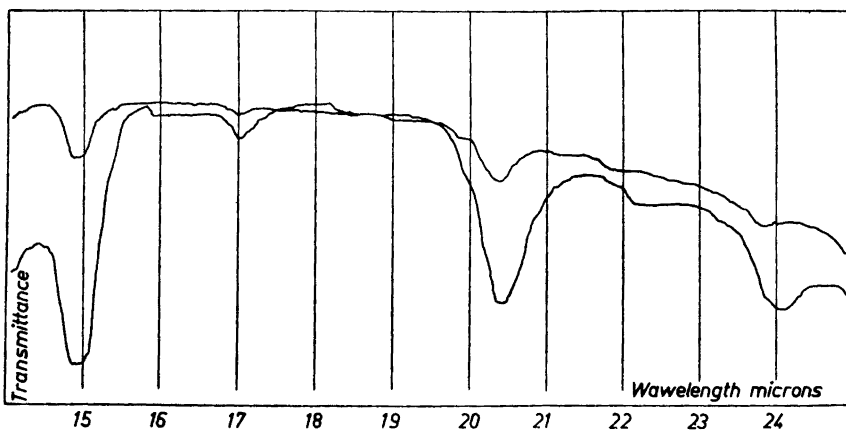


Fig. 3. IR absorption curve of the *cycloheptanone* derivative.

is tetragonal and it seems that the molecules in the crystal have the conformation C (Fig. 1). The *cyclopentanone* derivative (III) might possibly represent the conformation A. Both structures are comparatively simple.

The structure of the *cyclohexanone* derivative (II) is more complicated and the results obtained as yet do not permit any conclusions as to the conformation.

For the seven-membered sulphur-containing ring in the *cycloheptanone* derivative (IV) several conformations are possible. The preliminary data indicate that the structure is very complicated with a rather large unit cell.

Figs. 2 and 3 show the IR-spectra for the compounds II and IV in the region 14–25 μ , where the C—S and S—S bond frequencies should be located.

In the spectrum of the *cyclohexanone* derivative (Fig. 2), the band at 19.9μ might possibly be attributed to the S—S linkage; it should be said, however, that in our experience the S—S bands are in most cases broader and less distinct. Curiously enough there is no indication for a C—S band in the region $14\text{--}16 \mu$; the distinct band at 18.5μ must have another origin and might be due to structural vibrations. The non-appearance of the C—S frequency might perhaps be due to special symmetry conditions in the molecule.

In the spectrum of the *cycloheptanone* derivative, which is less symmetrical (Fig. 3), we find the C—S band at 14.9μ and the S—S band at 20.4μ . It is obvious that the sulphur-containing ring system is not the same in the two compounds. On the other side, there is no indication for the occurrence of a branched chain containing a coordinative or double sulphur-sulphur bond.

Preliminary IR-studies on the compounds I and III indicate that the acetone derivative (I) shows the normal C—S and S—S bonds, whereas they are missing in the spectrum of the *cyclopentanone* derivative (III). This is in agreement with the crystallographic results, according to which only the latter compound should have a ring conformation with a center of symmetry.

A more detailed discussion of the spectra should be postponed until the conformation of the rings is established by crystallographic methods.

EXPERIMENTAL

Cyclohexanone derivative (Bis-3,3,6,6-pentamethylene-1,2,4,5-tetrathiane). *Cyclohexanone* (0.1 mole) is left to stand with a concentrated solution of ammonium disulphide (0.25 mole) in a closed vessel with occasional shaking. Gradually the ketone layer sinks to the bottom and changes to a yellow mixture of smears and crystals. When no further change can be observed (after 4—5 days), the product is separated, washed with water and triturated with ethanol or methanol, which dissolves the smeary by-products leaving dry, pale yellow crystals. Repeated recrystallisations from ligroin and propanol, if necessary with charcoal, give a colourless product. Short-prismatic crystals with m. p. $130.5\text{--}131.5^\circ$. The compound is easily soluble in benzene, chloroform and carbon disulphide. (Found: C 48.9; H 6.87; S 44.07; mol.weight 293, 299, 286. Calc. for $C_{12}H_{20}S_4$: C 49.25; H 6.89; S 43.83; mol.weight 292.5).

Cycloheptanone derivative (Bis-4,4,7,7-hexamethylene-1,2,3,5,6-pentathiepane). *Cycloheptanone* (0.1 mole) was added to a solution of ammonium disulphide (0.25 mole) as described above. In this case the reaction proceeds more slowly and it is appropriate to shake the mixture on a machine for the first 10 h. After standing for about one week, the mixture is worked up as described above and the product recrystallised from propanol and ligroin. Colourless, thin needles with m. p. $127\text{--}128^\circ$, easily soluble in benzene, chloroform, and carbon disulphide. (Found: C 47.85; H 6.90; S 45.39; mol.weight 363, 340, 336. Calc. for $C_{14}H_{24}S_5$: C 47.68; H 6.86; S 45.46; mol.weight 352.6).

The *molecular weights* were determined by the boiling point method in benzene solution. Some experiments with the Rast method gave consistent results. The *IR-spectra* were recorded with a Perkin-Elmer model 21 double-beam spectrophotometer with a potassium bromide prism. The substances were studied in Nujol emulsions of two different concentrations.

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