

## The Acid-catalyzed Reaction between Chloroacetone or 1,3-Dichloroacetone and Hydrogen Sulfide

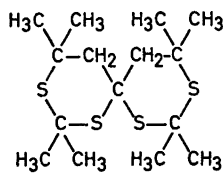
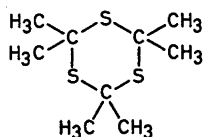
CHRISTOFFER RAPPE and ROLAND GUSTAFSSON

*Institute of Chemistry, University of Uppsala, Uppsala, Sweden*

By X-ray analysis it has been established that the product,  $C_6H_{10}S_3$ , formed when an alcoholic solution of chloroacetone saturated with hydrogen chloride was treated with hydrogen sulfide, has the structure 2,5-dimethyl-2,5-endothio-1,4-dithiane (V). The corresponding treatment of 1,3-dichloroacetone yielded the diethylketal of 1,3-dichloroacetone (VIII). When 1,3-dichloroacetone was treated with hydrogen sulfide in dilute hydrochloric acid, two products could be isolated and characterized: 1,15-dichloro-4,8,12-trithiapentadecane-2,6,10,14-tetraone (XII) and 1,5-dithiacyclooctane-3,7-dione (XIII).

The reaction between carbonyl compounds and hydrogen sulfide is very complex. A large number of different products can be isolated depending on the experimental conditions and the nature of the carbonyl compound used. The various products, which have been isolated are hydroxythiols, *gem* dithiols, thiones, trithianes, polysulfides,  $\alpha,\alpha'$ -dihydroxysulfides, enethiols, and unsaturated sulfides. For a recent review of this field, see Campaigne.<sup>1</sup> The initial product formed in many, if not all, of these reactions has been assumed to be the simple addition product, the hydroxythiol.<sup>1,2</sup>

From the reaction of acetone with hydrogen sulfide in acid medium, a crystalline compound ("tetrathioacetone",  $C_{15}H_{28}S_4$ ) has been isolated together with the main product, trithioacetone (I).<sup>3</sup> Recently the structure of this compound has been established as 2,2,4,4,8,8,10,10-octamethyl-3,5,7,9-tetrathiaspiro[5,5]undecane (II).<sup>4</sup>



In the cases where  $\alpha$ -halogeno carbonyl compounds take part in the reaction, the behaviour can be still more complex, because the number of possible centers for reaction increase.

The uncatalyzed reactions between some perhalo carbonyl compounds and hydrogen sulfide have been studied by Harris.<sup>5</sup> He has found that depending on the molar ratio (carbonyl compound/hydrogen sulfide) hydroxythiols or  $\alpha,\alpha'$ -dihydroxysulfides could be isolated from the reactions with chloral, perfluoroaldehydes, and perfluoroketones. In this reaction Harris suggests that the reaction is an attack by the hydrogen sulfide on the carbonyl group. The relatively high order of stability of the products is due to the highly electronegative perfluoroalkyl groups which hinder the leaving of a thiol or a hydroxyl group with its pair of electrons.<sup>5</sup>

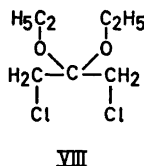
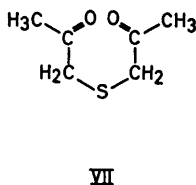
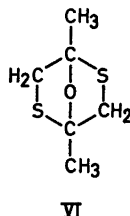
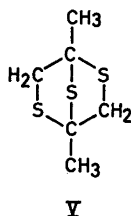
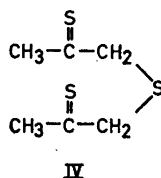
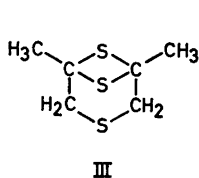
Up to now the reaction between an  $\alpha,\alpha'$ -dihaloketone and hydrogen sulfide seems not to have been studied. In the present investigation the products from the acid-catalyzed reaction between 1,3-dichloroacetone and hydrogen sulfide are studied. In connection with this work it was of interest to determine the structure of the products from the acid-catalyzed reaction between monochloroacetone and hydrogen sulfide, which still is unclear.<sup>6-9</sup>

*Monochloroacetone, hydrogen sulfide and hydrogen chloride.* In 1942 Böhme, Pfeifer and Schneider studied the reaction between monochloroacetone and hydrogen sulfide in an alcoholic solution saturated with hydrogen chloride. They isolated a product with the composition  $C_6H_{10}S_3$ , and since this product did not show any reactions for thiones, the authors proposed the structure 2,6-dimethyl-2,6-endothio-1,4-dithiane (III).<sup>6</sup>

In 1948 Brintzinger and Ziegler reported that they had prepared bis-thioacetyl sulfide (IV) from cold chloroacetone, hydrogen sulfide, and hydrogen chloride.<sup>7</sup> This assumption was based only on elementary analyses. Shortly after, Böhme and Schneider reported that although the boiling points were different for the products reported by them and by Brintzinger and Ziegler, these two products were identical and the correct structure would be III.<sup>8</sup>

However, the same year, Hromatka and Engel proposed that the correct structure for the product would be 2,5-dimethyl-2,5-endothio-1,4-dithiane (V).<sup>9</sup> This assumption was based on information from two experiments. Chloroacetone and sodium thiosulfate dissolved in concentrated hydrochloric acid was boiled for 15 min. Two products could be isolated, compound III (or V) and the oxygen analogue, 2,5-dimethyl-2,5-endoxy-1,4-dithiane (VI).<sup>9</sup> For a further discussion of the structure of the oxygen analogue, see Schotte.<sup>10</sup> The other reason was, that when bis-acetyl sulfide (VII) was treated with hydrogen sulfide no III (or V) could be isolated. Hromatka and Engel did not consider these indications as any final proof of the structure, and they left its determination to Böhme and Schneider.<sup>9</sup>

Recently the structure was studied by Olsson using NMR-technique.<sup>11</sup> The NMR-spectrum contained only two sharp singlets which gave no solution of the structural problem.<sup>11</sup> As comparison we studied the NMR-spectrum of the oxygen compound VI. Contrary to the sulfur analogue III (or V), VI gave one singlet and one AB-quartet ( $J_{gem} = 9$  cps,  $|\nu_A - \nu_B| = 11$  cps), the ratio of these two bands was 3:2. This is in harmony with structure VI.



This difference between the NMR-spectra of the sulfur and the oxygen compound can be interpreted in two ways. The two compounds can either have a pronounced difference in structure, *e.g.* III and VI. The other explanation is that due to difference in steric strain and electronegativity, the *exo*- and *endo*-protons are non-equivalent in the oxygen compound VI but equivalent in the sulfur analogue V. For a discussion of this topic, see Olsson and references therein.<sup>12</sup>

In order to obtain final proof of the structure an X-ray analysis was suggested by the present authors and performed by O'Connell. In this it was found that the correct structure is 2,5-dimethyl-2,5-endothio-1,4-dithiane (V). The X-ray data will be published elsewhere.<sup>13</sup>

*1,3-Dichloroacetone, hydrogen sulfide and hydrogen chloride.* The reaction was studied in two solvents: ethanol and water. In one experiment, where hydrogen sulfide was added to a chilled ethanolic solution of 1,3-dichloroacetone saturated with hydrogen chloride, the isolated product was the diethylketal of 1,3-dichloroacetone (VIII). It could be noted that under these conditions acetone yielded compounds I and II, and monochloroacetone compound V.

The formation of a ketal in the case of a dihaloketone while under the same conditions a monohaloketone gives a product of substitution can be explained on the basis of the observed greater stability of acetal-like compounds of

polyhalogeno aldehydes and ketones as compared with the unhalogenated species.<sup>5,14</sup> The hydrolysis of these halogenated species is extremely slow.<sup>15-17</sup>

Another question worth being discussed is the unreactivity of the chloro atoms in the ketal VIII. It is known that although the halogen in  $\alpha$ -haloketones is very reactive, the halogen of the ketals has the same reactivity as aromatic halogens.<sup>14</sup> Prjanischnikow and Leontowitsch, who studied the dimethyl ketal of 1,3-dichloroacetone, found that this compound reacted very slowly with silver at 160°C.<sup>17</sup> Thus it can be explained why in the present case no substitution occurred with hydrogen sulfide, which in strongly acid solution is a bad nucleophile.

In the other experiment, the ketalisation was hindered by the use of dilute hydrochloric acid as solvent. In this case two substances, A and B, could be isolated. The solution was kept at room temperature and hydrogen sulfide was passed through for some hours. At addition of water a voluminous precipitate was formed (substance A). The filtered aqueous solution was heated to boiling, chilled and extracted with ethyl acetate. After the ethyl acetate was evaporated another crystalline compound could be isolated (substance B).

Substance A was the main product and could be isolated in 61 % yield. Although it was repeatedly recrystallized from ethanol, it was not possible to obtain it in an analytically pure state (m.p. 92–94°C). The analytical figures gave the approximate empirical formula  $C_{12}H_{16}O_4S_3Cl_2$  ( $M = 391.4$ ). Since the compound decomposed at the melting point, molecular weight determinations performed by ebullioscopic and Rast's method gave inaccurate values. By mass-spectrometry the molecular weight could be determined as 390, 392,

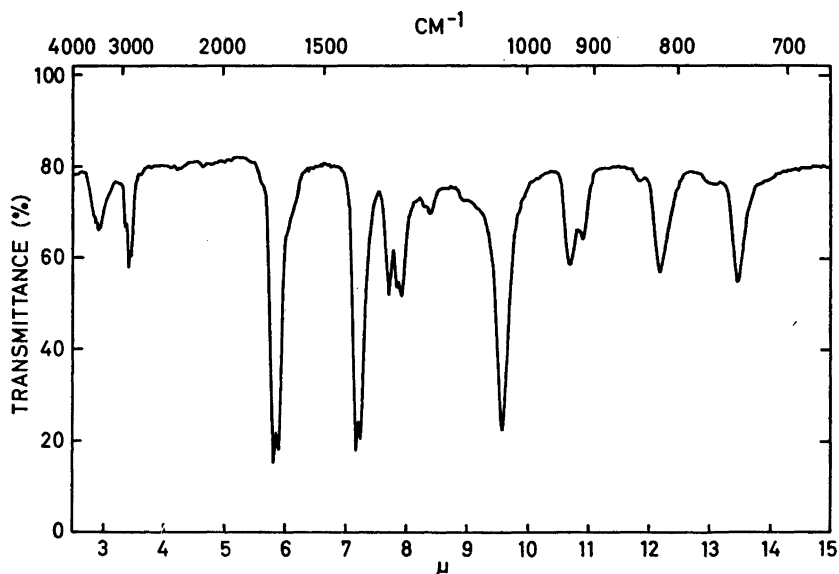


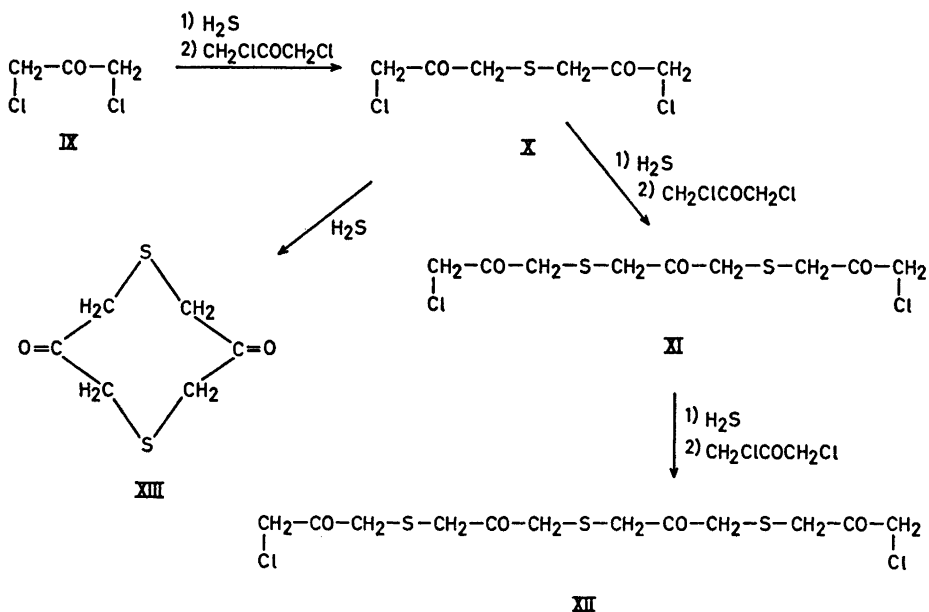
Fig. 1. Infrared spectrum of 1,15-dichloro-4,8,12-trithiapentadecane-2,6,10,14-tetraone (solid in KBr).

and 394 (the two chlorine isotopes 35 and 37 give three molecular peaks). From this it could be concluded that the suggested empirical formula was correct.

The infrared spectrum of substance A (Fig. 1) has two carbonyl bands, at  $1725\text{ cm}^{-1}$  and  $1700\text{ cm}^{-1}$ . It is found that in  $\alpha$ -haloketones halogen atoms result in an increase in the carbonyl frequencies of about  $20\text{ cm}^{-1}$ .<sup>18,19</sup> Thus the two carbonyl frequencies indicate that substance A has  $\alpha$ -halosubstituted keto groups.

The NMR-spectrum was recorded and it contained one singlet ( $\delta = 3.91$  ppm), and several peaks in the region  $\delta = 3.08 - 3.14$  ppm. The ratio of the two bands was 1:2.9.

From this it can be concluded that substance A is 1,15-dichloro-4,8,12-trithiapentadecane-2,6,10,14-tetraone (XII). The two chloromethyl groups were identical and gave the singlet at  $\delta = 3.91$  ppm, while the other methylene groups gave the complex band at  $\delta = 3.08 - 3.14$  ppm. The magnetic surroundings of these six groups are about the same, thus the peaks would be at the same field.



Scheme 1

It can be assumed that the formation of XII, which can be considered as a linear tetramer derivative of 1,3-dichloroacetone, takes place *via* the dimer X and probably also the trimer XI (see Scheme 1). Contrary to X and XI the larger molecule XII is so insoluble in the solvent that it precipitates. By warming, the formed precipitate goes into solution again.

Compound B was isolated only in an 11 % yield, and could be purified by recrystallization and sublimation (m.p. 145–146°C). The analytical data gave an empirical formula  $(C_3H_4OS)_n$  and by mass-spectrometry the molecular weight was determined to 173.6 ( $C_6H_8O_2S_2$ ).

The IR-spectrum (Fig. 2) had only one band at  $1725\text{ cm}^{-1}$  which showed that the substance contained a carbonyl group. The NMR-spectrum contained only one singlet ( $\delta = 3.73\text{ ppm}$ ), indicating that all methylene groups were equivalent. From these data it could be concluded that compound B was the cyclic dimer 1,5-dithiacyclooctane-3,7-dione (XIII).

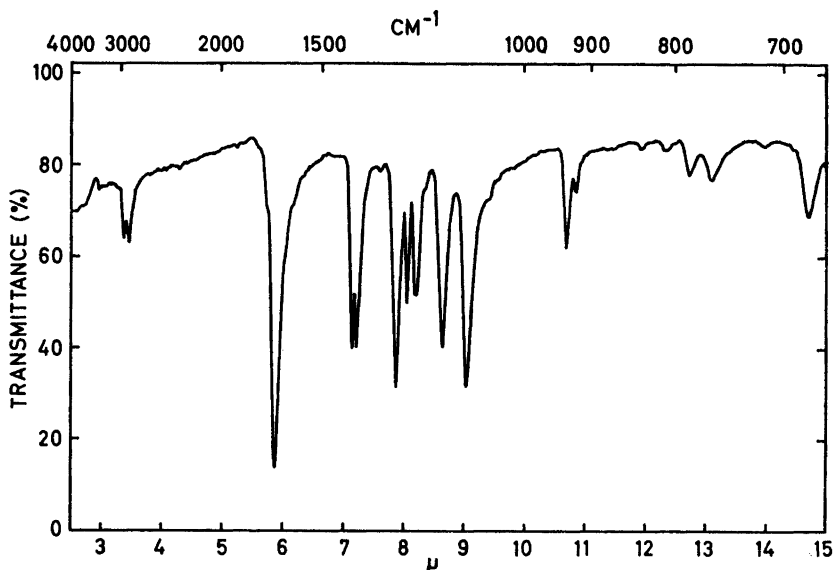


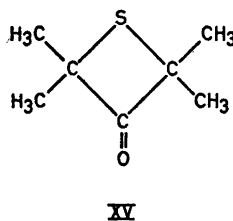
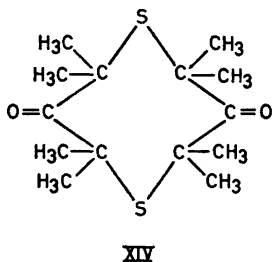
Fig. 2. Infrared spectrum of 1,5-dithiacyclooctane-3,7-dione (solid in KBr).

1,5-Dithiacyclooctane-3,7-dione (XIII) has the same precursor as XII, the dimer X (see Scheme 1). The dimer X can react with another molecule of X or another two molecules of 1,3-dichloroacetone, in both cases with the formation of the linear tetramer XII. Another possibility is that it reacts with itself under cyclization giving XIII.

If the reaction mixture was extracted without any prior heating, the cyclic compound XIII could also be isolated, but only in a 5 % yield, which indicated that heating increased the yield, but is not necessary.

This seems to be the first example where the ring system 1,5-dithiacyclooctane-3,7-dione has been prepared. In 1952 Schotte reported that he had isolated 2,2,4,4,6,6,8,8-octamethyl-1,5-dithiacyclooctane-3,7-dione (XIV) from the reaction of 2,4-dibromo-2,4-dimethylpentanone-3 and potassium hydrogen sulfide.<sup>20</sup> He came to this conclusion from a molecular weight determination according to Rast.<sup>20</sup> Later it was shown by Claeson, Thalén and Schotte that due to sublimation this determination of the molecular weight was incorrect,

and the correct structure of this compound was 2,2,4,4-tetramethyl-3-thietanone (XV).<sup>21</sup> It can be pointed out that due to sublimation a Rast determination of the molecular weight of 1,5-dithiacyclooctane-3,7-dione (XIII) gave the value 266 (calculated value 176.3).



In both compounds (XII and XIII), which can be isolated from the reaction between 1,3-dichloroacetone and hydrogen sulfide in aqueous acid media, the keto group had not reacted, while under similar conditions the keto group of acetone and monochloroacetone did react. As the keto group of a halogenated keto-compound is known to react more easily than that of an unhalogenated ketone (or aldehyde) this needs further explanation.<sup>5,15</sup> One explanation can be that in the aqueous solution 1,3-dichloroacetone forms a hydrate, which does not react or reacts slowly with hydrogen sulfide; *cf.* Ref. 2.

### EXPERIMENTAL

The NMR-spectra were recorded on a Varian A-60 spectrometer, the infrared spectra on a Perkin-Elmer, model 157 spectrometer. The NMR-spectra of liquids were taken on neat samples of crystalline compounds using trifluoroacetic acid as solvent.

*2,5-Dimethyl-2,5-endothio-1,4-dithiane* was prepared according to Böhme, Pfeifer and Schneider,<sup>6</sup> m.p. 46–47°C.

*1,3-Dichloroacetone, hydrogen chloride and hydrogen sulfide. A. Solvent ethanol.* A solution of 10.0 g (0.079 mole) of 1,3-dichloroacetone in 100 ml of absolute ethanol was saturated with dry hydrogen chloride. The solution was cooled in an ice-salt mixture and hydrogen sulfide was bubbled through for 5 h. The reaction mixture was poured on 200 g of ice, the crystals immediately filtered off. In this process 5.7 g of white crystals (m.p. 28.5–30.5°C) could be collected. After diluting, the aqueous solution was extracted with ether, the ethereal layer dried with magnesium sulfate and the ether evaporated. At this process, an additional 4.0 g of crystals was obtained (m.p. 27–29.5°C). Total yield 9.7 g (0.048 mole, 61 %) of the diethyl ketal of 1,3-dichloroacetone. By sublimation the m.p. could be raised to 31–32°C; Prjanischnikow and Leontowitsch quoted the m.p. 28°C.<sup>17</sup> (Found: C 41.49; H 6.85; Cl 35.21. Calc. for C<sub>7</sub>H<sub>14</sub>O<sub>2</sub>Cl<sub>2</sub>: C 41.81; H 7.01; Cl 35.26).

*B. Solvent diluted hydrochloric acid.* Hydrogen sulfide was bubbled through a solution of 10.0 g (0.079 mole) of 1,3-dichloroacetone in 100 ml of diluted aqueous hydrochloric acid (1:3) for about 5 h. An oily precipitate was filtered off and discharged (probably polymers). To the filtrate 100 ml of H<sub>2</sub>O was added and after some minutes a voluminous precipitate could be observed. After one night in a refrigerator 4.7 g (0.012 mole, 61 %) of crystals could be collected, m.p. 86–90°C. After several recrystallizations from ethanol the m.p. was raised to 92–94°C, but the substance 1,15-dichloro-4,8,12-trithiapentadecane-2,6,10,14-tetraone (XII) was not analytically pure. (Found: C 37.31; H 4.26; S 25.04; Cl 16.77; M. W. 390, 392, 394. Calc. for C<sub>12</sub>H<sub>16</sub>O<sub>4</sub>S<sub>3</sub>Cl<sub>2</sub>: C 36.83; H 4.12; S 24.58; Cl 18.12; M. W. 391.4).

The infrared spectrum of 1,15-dichloro-4,8,12-trithiapentadecane-2,6,10,14-tetraone is given in Fig. 1.

The filtrate was heated to boiling and was immediately chilled. The solution became red-coloured. It was carefully extracted with ethyl acetate and the extract dried ( $\text{MgSO}_4$ ) and evaporated. The residue was 0.8 g (0.0045 mole, 11 %) of faintly red-coloured crystals, m.p. 138–142°C. Recrystallization from acetone gave colourless flaky crystals of 1,5-dithiacyclooctane-3,7-dione (XIII) m.p. 143–145°C. After sublimation at 11 mm the m.p. was raised to 145–146°C. (Found: C 41.00; H 4.58; S 36.24; M. W. 176. Calc. for  $\text{C}_8\text{H}_2\text{O}_2\text{S}_2$ : C 40.89; H 4.58; S 36.38; M. W. 176.3). The infrared spectrum of 1,5-dithiacyclooctane-3,7-dione is given in Fig. 2.

*Acknowledgements.* The authors wish to express their thanks to Professor Arne Fredga for his interest in this work and for all facilities placed at their disposal. For the mass-spectra we are indebted to Docent Ragnar Ryhage, Laboratory of Mass spectrometry, Karolinska Institutet, Stockholm 60, and for the micro analyses to Dr. A. Bengtsson. A grant from the *Faculty of Mathematics and Natural Sciences* to one of us (R. G.) is gratefully acknowledged.

#### REFERENCES

1. Campaigne, E. In Kharasch, N. *Organic Sulfur Compounds*, Pergamon, Oxford 1961, Vol. I. p. 134.
2. Lienhard, G. E. and Jencks, W. P. *J. Am. Chem. Soc.* **88** (1966) 3982.
3. Baumann, E. and Fromm, E. *Ber.* **22** (1889) 2592.
4. Van Dort, H. M. and Mijs, W. J. *Rec. Trav. Chim.* **85** (1966) 15.
5. Harris, J. F., Jr. *J. Org. Chem.* **30** (1965) 2190.
6. Böhme, H., Pfeifer, H. and Schneider, E. *Ber.* **75** (1942) 900.
7. Brintzinger, H. and Ziegler, H.-W. *Chem. Ber.* **81** (1948) 380.
8. Böhme, H. and Schneider, E. *Chem. Ber.* **82** (1949) 208.
9. Hromatka, O. and Engel, E. *Monatsh.* **78** (1948) 38.
10. Schotte, L. *Arkiv Kemi* **3** (1951) 397.
11. Olsson, K., Baeckström, H. and Engwall, R. *Arkiv Kemi.* **26** (1966) 219.
12. Olsson, K. *Arkiv Kemi.* *In press.*
13. O'Connell, A. *Acta Cryst.* *To be published.*
14. Kühn, M. *J. prakt. Chem.* [2] **156** (1940) 103.
15. Bedoukian, P. Z. *J. Am. Chem. Soc.* **66** (1944) 1325.
16. Jacobsen, O. and Neumeister, R. *Ber.* **15** (1882) 599.
17. Prjanischnikow, N. D. and Leontowitsch, W. A. *Ber.* **68** (1935) 1866.
18. Bellamy, L. J. *The Infra-red Spectra of Complex Molecules*, Methuen, London 1958, p. 139.
19. Rappe, C. *Arkiv Kemi* **21** (1963) 503.
20. Schotte, L. *Arkiv Kemi* **5** (1953) 57.
21. Claeson, G., Thalén, A. and Schotte, L. *Arkiv Kemi* **21** (1963) 295.

Received December 5, 1966.