Table 2.

| | Crude product | | Theoretical data |
	No. 1	No. 2	
Equiw. weight	231	228	226
N %	0.9	0.8	—
C %	72.9	72.0	74.3
H %	4.3	4.3	4.4
Ash %	0.12	0.29	—

respectively. The average yield of crude product was 88 %.

Also tried was the oxidation of benzyltoluene according to this method, without excess of nitric acid. Using 91 g benzyltoluene and the equivalent amount of HNO_3 a temperature of 206° C and a pressure of 22 kg/cm² were reached. The reaction product was oily and could be separated into 26 g of solid material and 70 g of oil. After washing with benzene the solid material weighed 11 g and had the equivalent weight 237 and melting point 192—193° C. (Literature value for *p*-benzoylbenzoic acid 194° C.)

Finally some experiments were run with HNO_3 of 15 % concentration in a 50 % excess but this time the nitric acid was charged in two portions. Half of the acid was charged from the beginning and at 135—140° C the temperature and pressure began to rise quickly, the temperature reaching 180° C and the pressure 30—40 kg/cm² in a few minutes. When the temperature and pressure failed to rise any more but started to decrease, the other half of the nitric acid was placed into the autoclave and the temperature was brought up to about 200° C by external heating. The reaction was comparatively slow during this second phase. Operating this way an increase in capacity was possible. In each experiment 182 grams of benzyltoluene was oxidized in a 2.5 liter autoclave. The result of this series may be seen from Table 3. As usual the figures for temperature and pressure refer to maximal values.

Table 3.

| Temperature | Pressure | Yield | Equiv. weight | N (Dumas) |
°C	Kg/cm²	%		%
197	34	94.0	225.7	0.6
201	36	93.0	228.2	0.8
200	39	97.5	234.6	0.7
198	40	88.5	218.4	0.7

Such a crude acid mixture was purified with SO_2 in alkaline solution according to a procedure described in a previous paper [8] and was then free from nitro compounds. (Yield 79 %). It was heated (100 g) in 96 % H_2SO_4 at 130° C for 1 hour and after cooling the solution was diluted with water. After washing with water the precipitate was treated with Na_2CO_3. The part of the product which was not soluble in Na_2CO_3 was washed with water and dried. The melting point was 278° C. (Literature values for antraquinone 273—286° C.) Yield 41 g. The product was identified in ultraviolet spectrophotometer as antraquinone. The Na_2CO_3-solution was acidified with H_2SO_4 and 47 g of a product, melting at 190° C was obtained. (Literature value for *p*-benzoylbenzoic acid 194° C.)

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1,2-Dithiolane-3-carboxylic Acid

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As early as 1938 Fredga [1,2] had studied *a*,*a*'-dimercaptoadipic acid and its cyclic oxidation product 1,2-dithiane-3,6-dicarboxylic acid and pointed out the importance of studying aliphatic *a*,*a*'-dimercapto dicarboxylic acids and their oxidation to cyclic disulphides.

Schotte has continued the investigation and prepared 1,2-dithiolane-3,5-dicarboxylic acid (1,2-dithia*cyclo*pentane-3,5-di-

carboxylic acid) [3] and 1,2-dithia*cyclo*heptane-3,7-dicarboxylic acid [4].

The expectations of Fredga [1] have been realised by the discovery of "6-thioctic acid" (6,8-dithio-*n*-octanoic acid) and the important role this acid plays as a coenzyme [5] and in the photosyntheses [6]. It is the author's intention to synthesize lower homologues of 6-thioctic acid, to study the labile 1,2-dithiolane ring and to investigate the characteristics of these compounds as a function of the length of the side chain. The investigation is in progress. This publication deals with the synthesis of *rac.*-1,2-dithiolane-3-carboxylic acid and preliminary experiments on its optical resolution.

Methyl α,γ-dibromo-butyrate (prepared from α,γ-dibromo-butyryl bromide [7]) was treated with potassium thiol-acetate [8] and hydrolyzed with alkali to give α,γ-dimercapto-butyric acid. Oxidation of the mercapto-acid was carried out with iodine [9], oxygen [10] and hydrogen peroxide, but mostly polymeric products were formed. Experiments on oxidation to get a higher yield of the monomeric five-membered cyclic disulphide are in progress. The dithiolane-carboxylic acid was extracted with benzene in which the polymeric products are insoluble. Extraction with ether is unsuitable because part of the polymers is soluble in that solvent. The acid was obtained as a beautifully crystalline product of pale-yellow colour. On heating it is readily polymerized to a tough rubber-like mass. Attempts to distil the acid in vacuum also gave a polymeric mass.

Reduction of 1,2-dithiolane-3-carboxylic acid with zinc powder in ammoniacal solution yielded dimercapto-butyric acid. This indicates that the structure $\rangle S = S$ for the disulphide group is excluded.

1,2-dithiolane-3-carboxylic acid was obtained in two different crystalline forms having the melting points $80-82°$ and $147°$. Their ultraviolet absorption spectra are identical, with an absorption peak at 280 mμ, which means a shift from λ_{max} 330 mμ for 1,2-dithiolane and 6-thioctic acid. When another carboxylic group is inserted, the shift to shorter wavelengths is still greater. Schotte [11] has found that 1,2-dithiolane-3,5-dicarboxylic acid has λ_{max} 250 mμ.

The dissociation constant of the acid was preliminarily determined by measuring the pH of a solution of equivalent quantities of the acid and its sodium salt.
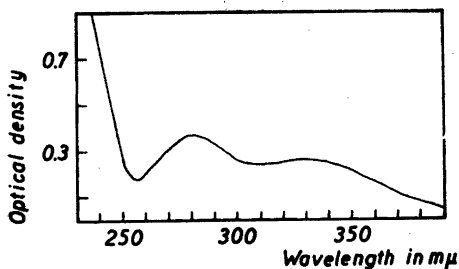

Fig. 1. *Ultraviolet absorption spectra of 1,2-dithiolane-3-carboxylic acid in 95 % ethanol, 1.55×10^{-3} M.*

Preliminary experiments on resolution have been carried out. With brucine and quinidine no crystals could be obtained and (+)-α-phenylethylamine gave a salt containing inactive acid. A dextrorotary acid was, however, obtained from the cinchonidine salt, crystallized from dilute alcohol. The mother liquor yielded crystals of different form containing excess of (−)-acid.

Experimental. Methyl α,γ-dibromobutyrate. The ester was obtained from abs. methanol and α,γ-dibromobutyryl bromide (B.p. 106—107°/9 mm. Plieninger gives no boiling point) in quantitative yield. B.p. 101—102°/9 mm.

Methyl-α,γ-di-thiolacetoxy-butyrate. 139 g of methyl α,γ-dibromobutyrate in 200 ml methanol was treated with an ethanolic solution of potassium thiolacetate prepared by neutralizing 90 g of thiolacetic acid with a solution of 66 g of potassium hydroxide in 200 ml methanol. There was an immediate precipitation of potassium bromide, which after standing overnight was filtered off and the methanol evaporated. Water was added, and the oil extracted with ether. The dried ethereal solution was evaporated and distilled to give 107 g (80 %) of pale yellow ester b.p. 178—179°/10 mm. About 10 gram distilled over below 178° and was shown to contain bromine.

α,γ-Dimercapto-butyric acid. 55 g of the ester was treated with 800 ml (675 ml of methanol and 125 ml of water) 2 N sodium hydroxide. After standing over-night, the methanol was distilled at 760 mm in nitrogen atmosphere in order to avoid oxidation. By treating the residue with dilute sulfuric acid and extracting with ether 38 g crude mercapto-acid was obtained as a yellow oil. The acid contained some acetic acid.

1,2-Dithiolane-3-carboxylic acid. The crude mercapto-acid was neutralized with 1 000 ml of dilute sodium-bicarbonate solution, and 2 ml 1 % ferric chloride was added, resulting in a solution of deep blue colour. With mechanical stirring and cooling with ice, 30 % hydrogen peroxide was added until the blue colour disappeared. The solution was acidified with sulfuric acid and extracted with benzene. (Part of the product was insoluble in benzene, but could be extracted with ether.) The benzene solution was dried and distilled. The crystallized residue weighed 5 g (15 % calculated on methyl a,γ-di-thiolacetoxy-butyrate). Recrystallization from *cyclo*hexane-benzol gave very pale yellow crystals m. p. 81—82°. (Found: Eq. wt. 150.6; S 42.61; Mol. wt. 147. Calc. for $C_4H_6O_2S_2$: Eq. wt. 150.2; S 42.69; Mol. wt. 150.2.) The molecular weight was determined ebullioscopically in acetone. From the acetone solution the acid was recovered as large crystals m. p. 147°.

Oxidation with gaseous oxygen using ferric chloride as catalyst and oxidation with iodine gave about the same yield as the peroxide oxidation.

Reduction. The polymeric acid was almost quantitatively reduced to the mercapto-acid with zinc powder [1]. (Titr. with NaOH and I_2 gave: Eq. wt. 152.8 and 160.1; Calc. for $C_4H_6O_2S_2$: Eq. wt. 152.2.)

Preliminary experiments on resolution. 0.15 g (0.001 mole) of rac. 1,2-dithiolane-3-carboxylic acid and 0.29 g (0.001 mole) of cinchonidine were dissolved in 2 ml ethanol and 1 ml water was added. Crystallization overnight yielded 0.20 g of salt. The acid was liberated from its salt in the usual manner. The rotatory power was measured in alcohol. M. p. 60—62°.

$$[a]_D^{25} = + 158°$$

Preliminary value of the dissociation constant. In a solution of 1.090×10^{-4} moles of 1,2-dithiolane-3-carboxylic acid and 1.090×10^{-4} moles of its sodium salt in 15 ml water the pH was found to be 3.42.

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Crystal Field Stabilization of First Transition Group Complexes

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The crystal field of Bethe [1] has been applied to the first transition group by Ilse and Hartmann [2], Santen and Wieringen [3] and Orgel [4]. Ballhausen and the present authors [5-8] have extended these applications, and in this communication special attention will be drawn to the energy decrease due to crystal field perturbations on complex ions with an unfilled 3d-shell.

Table 1 gives the data for crystal fields with cubic symmetry (originating from octahedral and tetrahedral complexes). In the cases where the complexes with different total spin quantum number are known, also the lowest value of S observed in complexes is considered. The stabilization parameter is defined: $\varrho = 2a - 3b$, where a is the number of γ_5- and b the number of γ_3-electrons in a strong crystal field of cubic symmetry [3,8]. The two states γ_5 and γ_3 of one d-electron have the energies E_2 and E_1 respectively [2]. The energy difference $(E_1 - E_2)$ in tetrahedral complexes [5] equals $-\frac{4}{9}(E_1 - E_2)$ in octahedral complexes. Thus, the tetrahedral configuration gives much lower crystal field influences than the corresponding octahedral configuration. The energy of the groundstate in terms of ϱ is decreased by $\frac{\varrho}{5}(E_1 - E_2)$ relative to a similar ion of spherical symmetry, *i. e.* a closed shell with $L = 0$. Since $(E_1 - E_2)$ in octahedral complexes in the first transition group is of the order of magnitude [6] 10 000 cm⁻¹