

## Short Communications

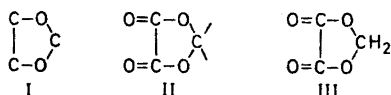
 Dioxolanones and Related  
Compounds

 I. Synthesis and Characterisation of  
Methylene Oxalate

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Oxalic acid, which has the grouping  $\text{HO}-\text{C}-\text{C}-\text{OH}$  in common with  $\alpha$ -diols and  $\alpha$ -hydroxy-acids, reacts like these substances<sup>1</sup> with carbonyl compounds to give the dioxacyclopentane or dioxolan ring I. The products with oxalic acid are the novel heterocyclic  $\alpha$ -diones of general formula II. These are cyclic oxalates of carbonyl hydrates and may be termed 1,3-dioxolan-4,5-diones or 2-oxo-3-oxabutanolides. The simplest member (III), here called methylene oxalate, is the simplest carboxylic diester possible.



Methylene oxalate (III) is easily prepared in good yield from oxalic acid and paraformaldehyde in concentrated sulphuric acid. It is isolated by extraction with dichloromethane and readily purified by recrystallisation or vacuum sublimation. The colourless crystals melt with sublimation at 166°C (only about 20° lower than anhydrous oxalic acid) and have a density of 1.6 g/cm<sup>3</sup>.

The mass spectrum (Fig. 1) has the parent peak at  $m/e$  101.9949  $\pm$  0.0005;  $\text{C}_2\text{H}_2\text{O}_4^+$  requires 101.9953. The small peak at  $m/e$  56 and a minute peak at 72 (seen only in the original spectrum) are assigned to  $\text{C}_2\text{O}_2^+$  and  $\text{C}_2\text{O}_3^+$  on the basis of accurate mass measurements.

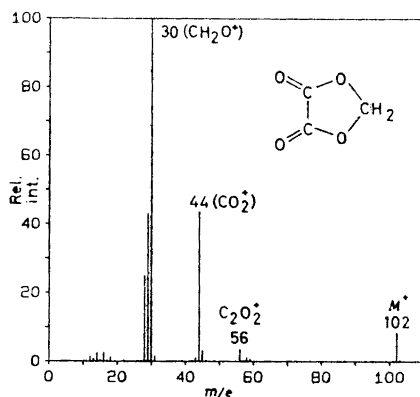


Fig. 1. Mass spectrum of methylene oxalate ionized by electron impact at 70 eV (ion source at ca. 150°C). The sample was eluted (by helium) from a gas-chromatographic column (2 m, ca. 6% high vacuum silicone grease at 100°C) directly into the spectrometer.

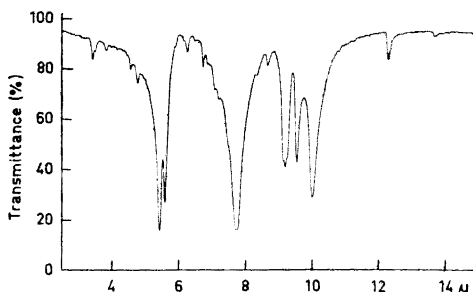


Fig. 2. Infrared spectrum of solid methylene oxalate in KBr.

The infrared spectrum (Fig. 2) of solid methylene oxalate has a strong carbonyl stretching band near 1845  $\text{cm}^{-1}$  (5.42  $\mu$ ) and a weaker band near 1792  $\text{cm}^{-1}$  (5.58  $\mu$ ). In dilute chloroform solution only the position of the weaker, low-frequency band

is markedly shifted, upwards to  $1812\text{ cm}^{-1}$  ( $5.52\ \mu$ ). The doublet has reversed intensities compared with the carbonyl bands of some saturated 5-membered cyclodiones of similar symmetry.<sup>2,3</sup> Succinic anhydrides<sup>2</sup> absorb at about the same mean frequency with larger splitting, and  $\alpha$ -diketones,<sup>3,4</sup> unable to enolize, absorb at lower mean frequencies with smaller splitting. In both cases<sup>2,3</sup> the high-frequency band is the weaker and in the cyclic anhydrides, where the carbonyl groups are nearly aligned, this band has been assigned to the symmetric vibration.<sup>2,5-7</sup> In the cyclic  $\alpha$ -diones, where the carbonyl groups form an angle smaller than  $90^\circ$ , the symmetric mode should be the more infrared active.<sup>8</sup> Consequently, the high-frequency band of methylene oxalate and the low-frequency band of the  $\alpha$ -ketones are both assigned to the symmetric vibration. This places methylene oxalate with the anhydrides in the small<sup>9</sup> group of known substances where the symmetric mode takes the higher frequency.<sup>10</sup>

The main C—O stretching band<sup>11</sup> occurs near  $1294\text{ cm}^{-1}$  ( $7.73\ \mu$ ), higher than is reported for most or all other saturated carboxylic alkyl esters. Methylene oxalate may also be unusual in combining high ester C—O and C=O stretching frequencies.<sup>11</sup>

The *proton magnetic resonance* signal from methylene oxalate in saturated chloroform-*d* solution appears at  $\delta\ 6.02$ ,  $\tau\ 3.98$ . The related 1,2-methylenedioxybenzenes absorb in the same region.<sup>12</sup>

*Experimental details.* A finely ground mixture of 38 g (0.3 mole) of oxalic acid hydrate and 10 g (ca. 0.3 mole) of paraformaldehyde was added to 100 ml of magnetically stirred concentrated sulphuric acid. Stirring was continued for 20 h in a stoppered flask and the resulting white suspension was transferred to an apparatus for continuous liquid-liquid extraction,<sup>13</sup> charged with 0.5 l of dichloromethane. To avoid foam from the acid carrying over into the extract, the apparatus had a minimum capacity of 0.25 l and was inclined with the side arm horizontal; if necessary a plug of glass wool was placed above the acid. After 5 h of vigorous boiling the dichloromethane extract was replaced by 0.5 l of fresh solvent and the extraction was continued for another 15 h. Occasionally a black tar appeared in the extract. After decantation and filtration through cotton wool, coloured impurities were removed by shaking with a

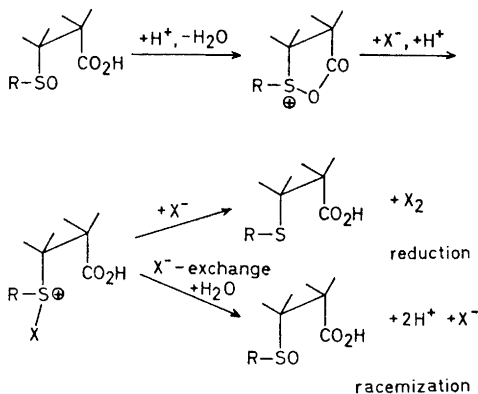
few grams of silicic acid. The yield of crude product varied somewhat and seldom was higher than 20 g (65 %). Recrystallisation, effected by dissolving the product (20 g) in 40 ml of hot acetone and adding 80 ml of dichloromethane, gave about 10 g of colourless methylene oxalate melting with sublimation at  $165\text{--}166^\circ\text{C}$  (on a Kofler bench). The m.p. was unchanged after sublimation at  $100^\circ\text{C}$  and 1 torr, or after recrystallisation from benzene, 600 ml of which dissolved 10 g at reflux and deposited 8 g of irregular crystals at room temperature. The density was found by flotation to be close to that of carbon tetrachloride in which the crystals were practically insoluble at room temperature.

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### Anchimerically Assisted Sulfoxide Reactions IV.

#### Neighbouring Group Participation in the Reduction of *syn*- and *anti-cis*-2-Benzylsulfinylcyclopentane-1-carboxylic Acid by Hydriodic Acid

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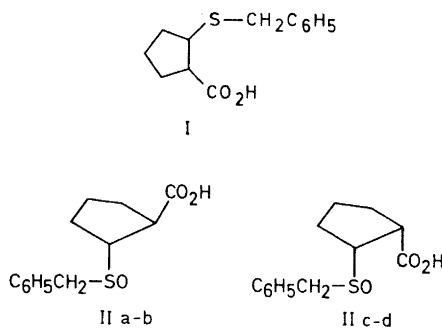
In earlier communications we have described the effect of anchimeric assistance in reduction<sup>1</sup> and racemization<sup>2</sup> of certain carboxylic substituted sulfoxides by hydriodic acid and hydrochloric or hydrobromic acid, respectively. The mechanism of the reaction was believed to involve a nucleophilic attack of the sulfinyl-oxygen upon the protonated carboxyl group with elimination of water to yield a cyclic acyloxysulfonium ion intermediate followed by fast halide ion attack upon the sulfur atom, leading to ring-opening.

In order to gain more information about structure-reactivity relationships<sup>1,3</sup> with respect to these reactions, we undertook a study on the reduction of all four (racemic) isomers of 2-benzylsulfinylcyclopentane-1-carboxylic acid.

The corresponding sulfide-acids (I) were prepared by the addition, in the presence of piperidine and Triton B,<sup>4,5</sup> of benzyl mercaptan to cyclopentene-1-carboxylic acid in benzene solution at 80°, resulting

in an approximately 3:1 mixture of two isomers with m.p. 54° (Ia) and 101° (Ib), respectively. The yield of crude I in this reaction was 70%. The favoured isomer Ia was assumed to be the *trans*-isomer, since Truce<sup>6,7</sup> has shown the nucleophilic addition of thiols to the cyclopentene ring system to be predominantly *cis*.

Oxidation of Ia with peracetic acid gave two sulfoxide isomers (IIa, m.p. 135° and IIb, m.p. 116.5°) which were separated by repeated recrystallization. Similarly, oxidation of Ib resulted in the isomers IIc, m.p. 156°, and IId, m.p. 164.5°.



When compounds IIa–d were studied kinetically under the same reduction conditions (0.5 M HClO<sub>4</sub>, 0.2 M NaI, 50% ethanol, 25.0°), it was found that IIc and IId were readily reduced, whereas IIa and IIb remained quite unchanged. As only reduction of the *cis*-isomers can be anchimerically accelerated in this case,