

## Short Communications

## Location of Double Bonds by Mass Spectrometry

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Many structural isomers with a double bond in different positions in an aliphatic chain have identical or almost indistinguishable mass spectra.<sup>1,2</sup> Moreover the dibromo and dichloro compounds formed from olefins by addition of halogen do not break characteristically between the halogen-bearing carbon atoms.\*\* It is possible, however, to determine the double bond position in methyl esters of long chain monounsaturated acids after addition of two deuterium atoms by means of deuteriohydrazine.<sup>3</sup> In the mass spectrum the positions of the deuterium atoms are indicated by  $m/e$  shifts in the series of ions  $[\text{CH}_3\text{O-CO}-(\text{CH}_2)_n\text{-}]^+$  ( $n > 1$ ) (I). The method suffers from complications caused by hydrogen-deuterium exchange reactions,<sup>4</sup> and by the formation of ions formally corresponding to (I) through reactions involving double cleavage and elimination of intermediate parts of the chain.<sup>5</sup>

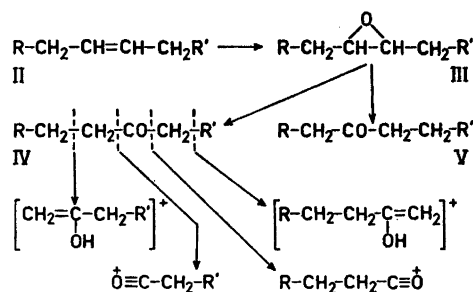
We now describe a method of transforming an olefinic compound into a derivative showing characteristic fragmentation in mass spectrometry. The olefin (II) is converted into the epoxide (III) and thence by the action of sodium iodide\*\*\* into a

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\*\* Unpublished experiments.

\*\*\* The mechanism and scope of this novel isomerisation of epoxides will be studied at Liverpool.

mixture of the two isomeric ketones (IV and V). The well-known  $\alpha$ - and  $\beta$ -cleavage of the ketones in mass spectrometry<sup>6</sup> gives rise to four fragments from each ketone (shown for one ketone only) and in addition  $\beta$ -cleavage towards an oxygenated functional group, as in fatty esters,<sup>7</sup> may produce a fifth characteristic fragment, (*viz.*  $\text{RCH}_2^+$ ).



The mass spectrum of the crystalline equi-molar mixture of methyl 9- and 10-oxodecanoates, obtained from methyl oleate without purification at either stage, shows ten major peaks assigned as follows;  $m/e$  141 10- $\alpha$ , 143 9- $\text{RCH}_2^+$ , 155 9- $\alpha$ , 156 10- $\beta$ , 157 10- $\text{RCH}_2^+$ , 170 9- $\beta$ , 185 9- $\alpha$ , 200 9- $\beta$ , 214 10- $\beta$ . The same product was obtained from methyl elaidate. So far the method has only been applied to long chain esters, but there does not seem to be any reason why it should not be general.

Epoxides were prepared by means of monoperphthalic acid.<sup>8</sup> Isomerisation was accomplished quantitatively in a mixture of methyl iodide and dimethylformamide (*e.g.* 5 mg of epoxide, 40 mg sodium iodide, 2 ml methyl iodide, 2 ml dimethylformamide, 4 h reflux). Methyl ethyl ketone and acetonitrile are alternative solvents, in which isomerisation is rather slower.

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## An X-Ray and Neutron Diffraction Study of Metacinnabarite

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The crystal structure reported earlier in the literature <sup>1,2</sup> of HgS (metacinnabarite), which is isotopic with ZnS (blende), has been confirmed by means of X-ray single-crystal and neutron powder diffraction data.

A native crystal of metacinnabarite, kindly supplied by Professor Gavelin of the Mineralogical Institute, University of Stockholm, was investigated by means of Weis-

senberg photographs, registering the reflections of the zones 0-4 around the axis [110] CuK $\alpha$  radiation was used. The Laue symmetry  $m\bar{3}m$  and the space group  $F\bar{4}3m$  (No. 216 in the *International Tables* <sup>3</sup>) were confirmed from the intensities of the reflections and the systematic extinctions found in the photographs.

Two possibilities for the structure of metacinnabarite were compared by the least-squares treatment of the intensity data:

Space group  $F\bar{4}3m$  (No. 216); (0,0,0;0, $\frac{1}{2}$ , $\frac{1}{2}$ ; $\frac{1}{2}$ ,0, $\frac{1}{2}$ ; $\frac{1}{2}$ , $\frac{1}{2}$ ,0) +  
 A) 4 Hg in 4(a) 0,0,0; 4S in 4(c)  $\frac{1}{2}$ , $\frac{1}{2}$ , $\frac{1}{2}$  and  
 B) 4 Hg in 4(a) 0,0,0; 4S in 4(b)  $\frac{1}{2}$ , $\frac{1}{2}$ , $\frac{1}{2}$ .

The structural possibility *A* is the one derived by v. Olshausen <sup>1</sup> and by Goldschmidt <sup>2</sup> from X-ray powder data, viz. a zinc blende structure with an Hg-S distance of 2.54 Å. The possibility *B* should give the mercury atom a six-coordination similar to the one present in cinnabar <sup>4</sup> and a distance Hg-S of 2.93 Å. It might be noted, however, that a deformed octahedron around the mercury atom with a pair of short Hg-S bonds (*sp*) as in cinnabar is incompatible with the cubic symmetry, found from both the X-ray single-crystal photographs and from the neutron powder data, *v. infra*. The interatomic distances Hg-S actually found in cinnabar are 2.36, 3.10, and 3.30 Å. The following results were obtained from the least-squares calculations:

$$\begin{aligned} A) R &= 6.9 \%, B_{\text{Hg}} = 3.92 \pm 0.07 \text{ \AA}^2, \\ &B_{\text{S}} = 2.03 \pm 0.34 \text{ \AA}^2 \\ B) R &= 20.6 \%, B_{\text{Hg}} = 3.02 \pm 0.14 \text{ \AA}^2, \\ &B_{\text{S}} = 13.78 \pm 1.92 \text{ \AA}^2 \end{aligned}$$

As seen from the temperature factors of the atoms and the discrepancy factors, the structure possibility *B* is definitely excluded by this study.

For case *A*, however, the outcome of the refinement is adequate. The shifts in the temperature factors at the final cycle of refinement were small and the weight analysis is satisfactory. The analysis of the weighting scheme and the list of observed and calculated structure factors will be reported elsewhere.<sup>5</sup>

The cell edge of a synthetic sample of metacinnabarite was found to be  $a = 5.8717 \pm 0.0005$  Å from X-ray Guinier powder data. The list of  $\sin^2 \Theta$  (obs.) and  $\sin^2 \Theta$  (calc.) will be given elsewhere.<sup>5</sup>