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1,3-DITHIOLANE DERIVATIVES FOR GAS CHROMATOGRAPHIC AND GAS CHROMATOGRAPHIC-MASS SPECTROMETRIC DETERMINATION OF ACYCLIC CARBONYL COMPOUNDS

TIMOTHY G. HARVEY and TREVOR W. MATHESON*

Catalysis and Surface Science Laboratory, CSIRO Division of Materials Science, University of Melbourne, Parkville, Victoria 3052 (Australia)

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SUMMARY

Acyclic carbonyl compounds react with ethane dithiol to give almost quantitative yields of the 1,3-dithiolanes. The derivatives are stable and are readily separated by gas chromatography. Diagnostically useful fragments are obtained on electron impact. These properties make 1,3-dithiolanes suitable for the characterization of acyclic carbonyls by gas chromatography-mass spectrometry.

INTRODUCTION

Aldehydes and ketones are important constituents in such diverse materials as essential oils, exhaust pollutants, food flavour and aromas, tobacco smoke, atmospheric smog and synthetic fuels. They are relatively volatile and heat stable so their separation and characterization by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) is generally uncomplicated. However, there are circumstances when the identification of these compounds is not straightforward. In many instances the carbonyl-containing material is present in minor amounts and/or is highly volatile; or the carbonyl function is part of a long chain and becomes difficult to distinguish from a hydrocarbon by MS¹. A standard method of overcoming these difficulties is to form derivatives of the carbonyl functional group, so small amounts can then be isolated from mixtures and concentrated, the volatility of the compounds altered, and chemical differences highlighted. In addition, selection of the appropriate derivatizing agent provides the option of using element specific GC detectors.

Many derivatization schemes utilize the ability of the carbonyl function to form imine (>C=N-) linkages. The most commonly employed carbonyl derivatives are the 2,4-dinitrophenylhydrazones (2,4-DNPH)²⁻⁶. Other common carbonyl derivatives used to assist in the analysis of aldehydes and ketones are the oximes, including methyloximes^{7,8}, benzyloximes⁸⁻¹⁰, *p*-nitrobenzyloximes⁹ and pentafluorobenzyloximes¹¹. However, these derivatives are not without fault, and problems associated with them include high molecular weight¹² (which limits both volatility and solubil-

ity), instability under gas chromatographic conditions² and lengthy preparative procedures^{5,9,11}. In addition, these hydrazone^{4,6} and oxime⁹⁻¹¹ derivatives can form *syn*- and *anti*-isomers which can be resolved by modern chromatographic techniques and thus add to the complexity of the analysis.

Of the other derivatives which can be formed with the carbonyl group, those which contain sulphur offer many advantages over hydrazone and oxime derivatives. The desirable features of sulphur derivatives with respect to MS have been noted in their application to carbohydrate chemistry^{14,15} and there are examples of the successful gas chromatographic separation of sulphur¹² and trimethylsilylated sulphur^{16,17} derivatives. 1,3-Dithiolane derivatives are used extensively for the protection of carbonyl groups¹³ but normally are not used for the spectroscopic characterization of carbonyl-containing material.

In this paper we report the preparation, chromatographic separation and mass spectroscopic analysis of a wide range of acyclic carbonyl compounds derivatized with ethane dithiol.

EXPERIMENTAL

Reagents

Ethane dithiol (Aldrich), boron trifluoride etherate ($\text{BF}_3 \cdot \text{Et}_2\text{O}$) (Eastman) and diethyl ether (Mallinckrodt; Nanograde quality) were used as received.

Carbonyl compounds were obtained from various sources and were not purified further, although their purity was checked prior to use (GC).

Preparation of derivatives

Solid carbonyl compounds were taken up in twice the minimum volume of ether required for complete dissolution and ethane dithiol added in slight molar excess. Liquid carbonyl compounds were combined with an equal volume of ether and half volume of ethane dithiol. $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (ca. 45% BF_3 , w/w) added in each case was approximately twice the volume of ethane dithiol present. The reaction was allowed to proceed at room temperature for 1-1.5 h, then stopped by careful addition of a saturated solution of sodium bicarbonate. In this time conversion for all chain lengths was virtually quantitative (as measured by GC). When carbon dioxide evolution had ceased completely, the derivative was extracted into a small amount of ether and the solution chromatographed directly. The derivatives can be stored for long periods without significant decomposition.

GC and GC-MS

Preliminary GC analyses were carried out on a Varian Model 3700 instrument using flame ionization detection. GC-MS analyses were carried out on a Hewlett-Packard 5995A instrument. Silica BP-1 WCOT columns (12 and 50 m, supplied by SGE, Melbourne, Australia) were used.

RESULTS AND DISCUSSION

Although the reaction conditions for the derivatization are extremely mild the conversions obtained were almost quantitative for all carbonyl compounds tested

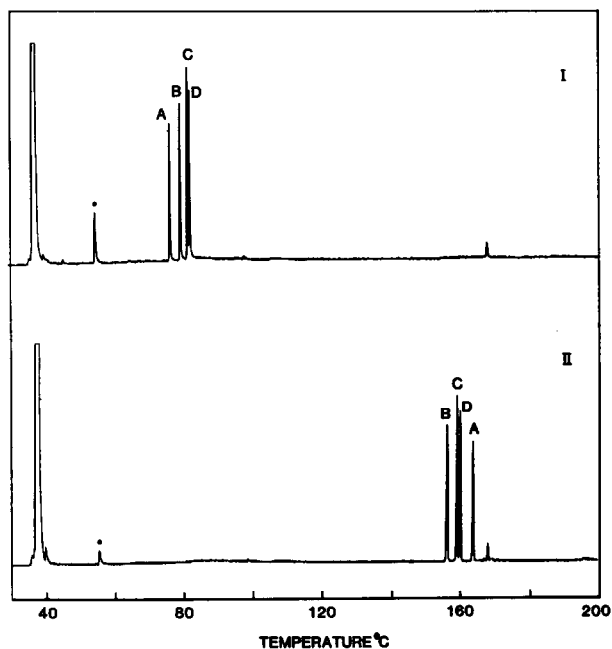
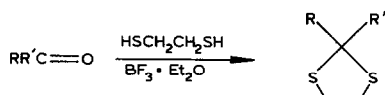


Fig. 1. GC traces of (I) the parent carbonyls and (II) the 1,3-dithiolane derivatives: A, octanal; B, 4-octanone; C, 3-octanone; D, 2-octanone. · Ethane dithiol.

(Table I). In neat ethane dithiol some long chain carbonyl compounds showed little or no reaction even though it has been recommended as an effective solvent for this derivatization¹⁸. The use of diethyl ether as solvent, together with minimal amounts of the dithiol obviates this problem. The products are stable under GC conditions and are eluted well after excess dithiol and any remaining carbonyl compound. Typical separations of a mixture of the derivatives of the four nC_8 -compounds are shown in Fig. 1. The mass spectra of the derivatives of octanal and the three n -octanones are given in Fig. 2; other compounds derivatized are listed in Table I.

The 1,3-dithiolane derivatives have relatively simple mass spectra which follow simple correlations normally observed in electron impact fragmentation. In all cases the molecular ion is of appreciable size, although predictably the relative intensity decreases as the chain length increases (Table I). This contrasts with the lack of molecular ions observed in cyclic sulphur derivatives of carbohydrates¹⁴. The mass spectra generally are dominated by base peaks at m/e 105, 119... due to the loss of alkyl substituents from the 2-position (Scheme 1). Thus the aldehydes show a base peak at m/e 105, 2-ones at 119, 3-ones at 133 and 4-ones at 147. As the substituents in the 2-position approach each other in length, competitive loss becomes more apparent (*cf.* 3-octanone, 4-octanone; Fig. 2). In compounds with branching in the substituent chain there is little effect on the fragmentation or the intensity of the



Scheme 1.

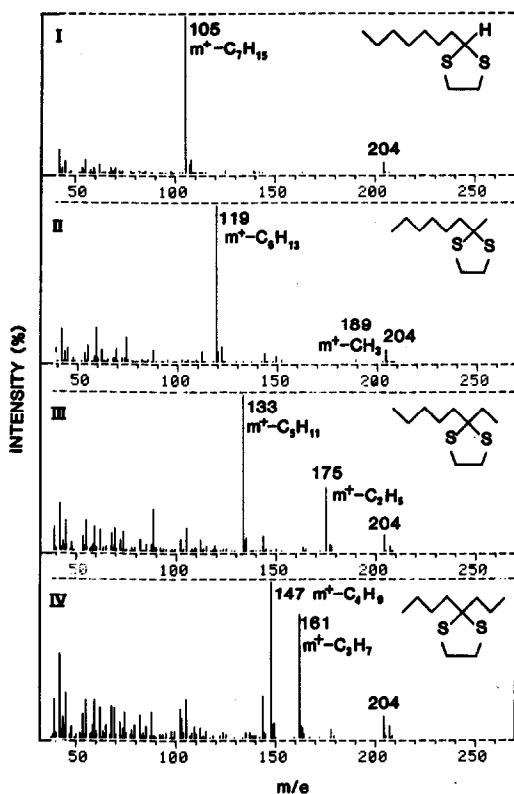


Fig. 2. Mass spectra (electron impact, 70 eV) of the 1,3-dithiolane derivatives of I, octanal; II, 2-octanone; III, 3-octanone; IV, 4-octanone.

TABLE I

CARBONYL COMPOUNDS DERIVATIZED WITH ETHANE DITHIOL

Numbers in parenthesis are % intensities of parent ions of derivatives.

| <i>m/e</i> 105* | <i>m/e</i> 119* | <i>m/e</i> 133* | <i>m/e</i> 147* |
|------------------|---------------------------|----------------------------|-------------------|
| Propanal (36%) | 2-Propanone (21%) | 3-Pentanone (12%) | 4-Octanone (12%) |
| Butanal (21%) | 2-Butanone (16%) | 3-Hexanone (14%) | 4-Decanone (6%) |
| Isobutanal (19%) | 2-Pentanone (20%) | 3-Heptanone (11%) | 4-Dodecanone (3%) |
| Pentanal (16%) | 2-Hexanone (12%) | 3-Octanone (9%) | |
| Hexanal (10%) | 2-Heptanone (10%) | 3-Nonanone (6%) | |
| Heptanal (9%) | 2-Octanone (7%) | 3-Decanone (4%) | |
| Octanal (4%) | 2-Nonanone (6%) | | |
| Nonanal (8%) | 2-Decanone (5%) | <i>m/e</i> 175 | |
| Decanal (6%) | 2-Undecanone (5%) | 3-Methyl-4-nonanone (1%) | |
| Undecanal (4%) | 2-Dodecanone (5%) | | |
| Dodecanal (4%) | 2-Tridecanone (1.5%) | | |
| | 2-Nonadecanone (0.5%) | <i>m/e</i> 189 | |
| | 2-Methyl-5-hexanone (11%) | 2-Methyl-3-nonanone (1.5%) | |
| | 2-Methyl-6-heptanone (6%) | | |

* Major diagnostic peak.

molecular ion except when the branching is α - to the dithiolane ring. When this occurs, the α -branched group is more easily lost than an unbranched chain of greater length and the intensity of the molecular ion decreases. Thus, the simple electron impact MS of these derivatives provides information on the location of the carbonyl group in the original compound.

1,3-Dithiolane derivatives of acyclic carbonyl complexes offer many advantages over hydrazone and oxime derivatives. They are easily and quickly prepared in high yield. Their stability and volatility gives them excellent GC properties. The components do not possess steric isomers and the presence of sulphur allows selective GC detection by flame photometric detection. The presence of molecular ions in the electron impact mass spectra facilitates compound identification and the simple fragmentation pattern enables determination of the ketonic (or aldehydic) alkyl substituents.

ACKNOWLEDGEMENT

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