Reaction Gas Chromatography/Mass Spectrometry

4—Structure Elucidation of Cyclic Sulphides by Gas Chromatography/Mass Spectrometry with the Use of On-line Hydrodesulphurization†

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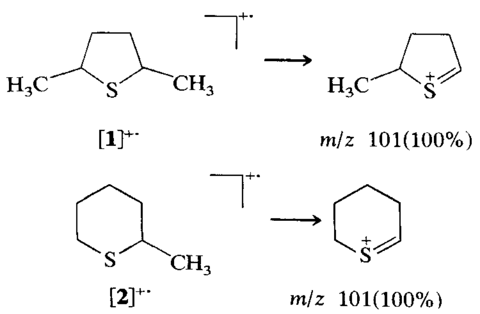
A method for structure determination of cyclic sulphides within mixtures is described. It involves the use of a vapour phase hydrodesulphurization micro-reactor (Raney nickel) located between the chromatographic column and the mass spectrometer (hydrogen and deuterium are used as carrier and reagent gases). A comparative examination of the mass spectra of the cyclic sulphides, as well as of the hydrocarbons and their deuterio analogues (deuterium atoms are bonded to carbon atoms which had been attached to sulphur) derived from the sulphides under the catalytic conditions employed, permits unambiguous determination of the size of the heterocycle and the position of the substituents.

INTRODUCTION

We have shown recently that reaction gas chromatography/mass spectrometry (GC/MS) which is based on the use of on-line vapour phase micro-reactors facilitates direct mass spectrometric investigation of olefins,[2] aliphatic alcohols[3] and cyclopropane compounds.[1] Now we have also studied another type of compound, cyclic sulphides, whose mass spectra are insufficiently informative and, in particular, do not always allow the determination of the size of the heterocycle and the position of the substituents.[4] For example, such a situation is demonstrated by the mass spectra of 2,5-dimethylthiolane (**1**) and 2-methylthiacyclohexane (**2**) (see Fig. 4(a) and (b)) whose differentiation is not practically possible if the only fragmentation regularities are used and the spectra of reference compounds are not available (see Scheme 1).



Scheme 1

Reaction gas chromatography was developed quite a long time ago as an analytical technique for structure determination of sulphides. Its application was based on catalytic desulphurization of such compounds in the on-line vapour phase micro-reactors (Pd/Al_2O_3 or Raney nickel) located between the injection port and the chromatographic column.[5,6] However, this method does not allow the determination of the size of the heterocycle and gives limited information regarding the substitution in the cycle. It should also be noted that reaction gas chromatography does not permit the differentiation of those thiacyclanes which are converted into identical hydrocarbons during the desulphurization (as is the case for **1** and **2**).

For on-line catalytic conversion of cyclic sulphides in reaction GC/MS, we also decided to apply hydrodesulphurization. It seemed, however, more efficient to locate a micro-reactor between the column and the mass spectrometer, but not before the column. The advantage of the former position is that the chromatograms registered correspond to those of the original mixtures (which secures their quantitative treatment), whereas the mass spectra correspond to the hydrocarbons whose mass spectra provide the additional information regarding the structure of the original sulphides. With the aid of this method, those isomeric thiacyclanes which form identical hydrocarbons during desulphurization can be distinguished. The additional spectral data needed for structure elucidation of sulphides can be deduced from the mass spectra of the corresponding dideuterioanalogues (in which the carbon atoms originally attached to sulphur atoms are now labelled with deuterium), obtained under the same conditions except that deuterium is used instead of hydrogen.

RESULTS AND DISCUSSION

For vapour phase desulphurization of cyclic sulphides in a micro-reactor located between the column and the

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† For Part 3, see Ref. 1.

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mass spectrometer, the same catalysts which are employed in reaction gas chromatography (for instance, Pd/Al_2O_3 or Raney nickel) may be used.[5,6] The only problem is to choose catalytic conditions for deuteriodesulphurization where isotope scrambling will be minimized. Both Raney nickel and Pd/Al_2O_3 catalysts operated at 150–250 °C give rise to extensive isotope scrambling if the reaction takes place in the presence of deuterium and Pd/Al_2O_3 catalyst becomes inactive at lower temperatures. The use of Raney nickel operated at 20–80 °C appears to be optimum. Under such conditions, deuteriodesulphurization of cyclic sulphides provides dideuteriohydrocarbons of high isotopic purity accompanied by a small quantity of d_1, d_3 and d_4 species. The mass spectra thus registered are quite interpretable and give very valuable information regarding the structure of the sulphides.

Chromaton W (120 mesh) coated with the dispersion of Raney nickel in Apiezon L was prepared by the method given in Ref. 6. The catalyst was placed in the micro-reactor located between the chromatographic column and the mass spectrometer. Prior to analysis, the catalyst was activated at 200 °C in the flow of hydrogen (or deuterium respectively) for 1–2 h. A plug of the catalyst 2 mm in diameter and 5–10 mm in length achieved quantitative desulphurization of 0.01–0.05 μl of an individual cyclic sulphide. The micro-reactor included a system allowing the compounds to by-pass the catalyst.

For gas chromatographic separation of cyclic sulphides, a column (3 m × 3 mm) containing 10% ethylene glycol adipate coated on 150 mesh Spherochrom was used. Hydrogen and deuterium were used as carrier and reagent gases.

It should be mentioned that the catalyst used can operate at temperatures up to 200 °C and, hence, different mono- and poly-cyclic sulphides may be subjected to hydrodesulphurization in the presence of hydrogen. At high catalyst temperatures, the retention times of components remain practically unaffected and broadening of chromatographic peaks is not observed.

Desulphurization in the presence of deuterium requires the temperature in the catalytic zone to be lower than 80 °C. In this case, broadening of the chromatographic peaks and, hence, decrease in resolution are observed even for low molecular weight compounds. This is supported by comparison of the chromatograms for artificial mixtures of monocyclic sulphides obtained through by-pass (Fig. 1(a)) and by using the desulphurization micro-reactor at a catalyst temperature of 80 °C (Fig. 1(b)). Broadening of chromatographic peaks becomes particularly significant when the retention times of the components are increased.

Analysis by the above-described method may be accomplished as follows. Firstly, the chromatogram and the mass spectra are registered for the mixture of sulphides to be studied with the use of the by-pass system. In two further stages the components of the mixture are passed over the catalyst in the presence of hydrogen and deuterium successively.

For mass spectrometric location of the label in deuterated alkanes the fragments arising from the loss of small alkyl radicals should be used, since these reactions are normally due to simple carbon–carbon bond cleavages. The fragments formed from the loss of large radicals are usually of little use since they can arise from rearrangement processes.

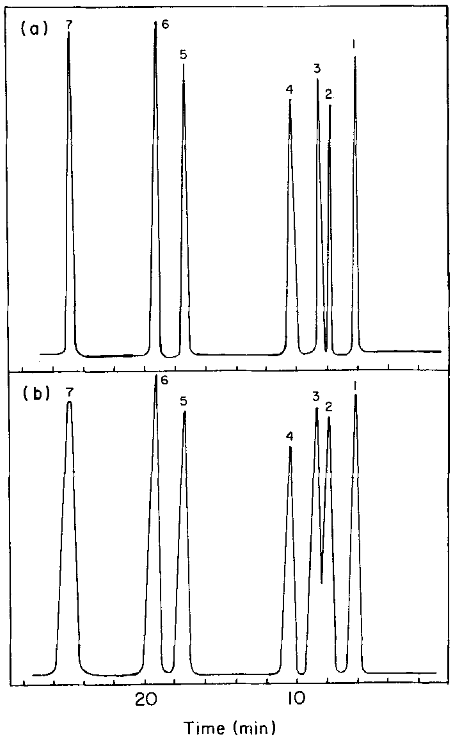

Figure 1. The chromatograms of mixtures obtained through by-pass (a) and by using the micro-reactor (Raney nickel) between the column and the mass spectrometer (b) (temperature of the column and the micro-reactor 80 °C, carrier gas deuterium 20 cm^3/min). (1) 2,5-Dimethylthiolane, (2) 3-methylthiolane, (3) 2-methylthiacyclohexane, (4) 4-methylthiacyclohexane, (5) 2-*n*-butylthiolane, (6) 2-*n*-propylthiacyclohexane, (7) 3-*n*-butylthiacyclohexane.

Hydrodesulphurization of thiolane and thiacyclohexane leads to *n*-butane and *n*-pentane, respectively (Figs 2 and 3). If the reaction proceeds in the presence of deuterium, labelled hydrocarbons are formed which contain deuterium atoms at terminal carbon atoms. Actually, their mass spectra (Figs 2(c) and 3(c)) reveal the single peaks for the $[M-CH_2D]^+$ ions.

Figures 4(a) and (b) shows the mass spectra of 2,5-dimethylthiolane and 2-methylthiacyclohexane which are practically indistinguishable if the spectra of reference compounds are not available. In both cases, hydrodesulphurization gives rise to *n*-hexane (Fig. 4(c)). At the same time, desulphurization in the presence of deuterium leads to dideuterio analogues whose mass spectra readily permit the determination of the position of the deuterio label and, hence, the structures of the sulphides. Since the spectrum of the deuteriated hydrocarbon (Fig. 4(d)) obtained from 2,5-dimethylthiolane displays singlets for the $[M-CH_3]^+$ and $[M-C_2H_4D]^+$ ions, this proves that it corresponds to 2,5-dideuteriohexane. In contrast, the mass spectrum of the deuteriated hydrocarbon (Fig. 4(e)) obtained from 2-methylthiacyclohexane shows a doublet for the $[M-CH_3]^+$ and $[M-CH_2D]^+$ ions and a singlet for the $[M-C_2H_4D]^+$ ion. This mass spectral

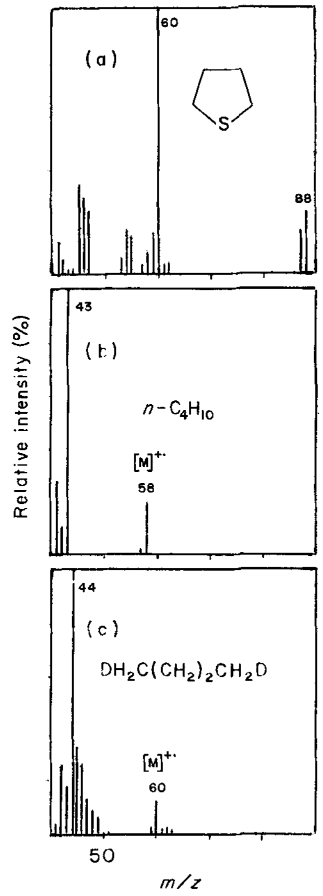

Figure 2. The mass spectra of (a) thiolane, (b) *n*-butane and (c) 1,4-dideuteriobutane.

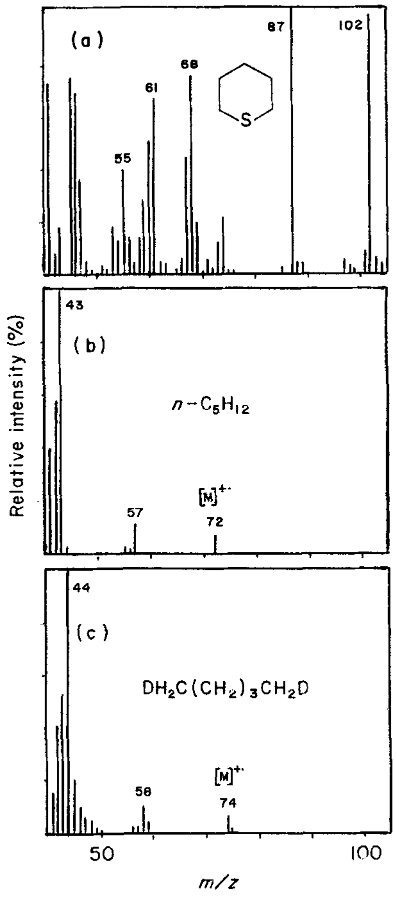

Figure 3. The mass spectra of (a) thiacyclohexane, (b) *n*-pentane and (c) 1,5-dideuteriopentane.

picture is peculiar to 1,5-dideuteriohexane. These two examples illustrate the great potential of the described method when similar isomers are to be distinguished.

Hydrodesulphurization of 3-methylthiolane (Fig. 5(a)) results in formation of 2-methylbutane (Fig. 5(b)), the main fragmentation of which occurs at branched positions (formation of the $[M-CH_3]^+$ and $[M-C_2H_5]^+$ ions). On passing to the corresponding dideuterio analogue (Fig. 5(c)), the formation of the doublet of the $[M-CH_3]^+$ and $[M-CH_2D]^+$ ions as well as the singlet of the $[M-C_2H_4D]^+$ ion takes place. This proves unambiguously that the labelled hydrocarbon responsible for the above spectrum is 1,4-dideuterio-2-methylbutane and, hence, that the original sulphide was 3-methylthiolane.

With the aid of the described method, the structure of 4-methylthiacyclohexane is established less distinctly. Its hydrodesulphurization leads to 3-methylpentane (Fig. 6(b)), which forms under electron impact the diagnostically important ions $[M-CH_3]^+$ and $[M-C_2H_5]^+$ (both ions are due to fragmentation at branched carbon atoms). The mass spectrum of the deuteriodesulphurization product (Fig. 6(c)) shows the $[M-CH_3]^+$ and $[M-CH_2D]^+$ ions which could be characteristic of 1,5-dideuterio- and 1,4-dideuterio-3-methylpentanes. So, on the basis of these data only, the structure of 4-methylthiacyclohexane or 2,3-dimethylthiolane could be assigned to the sulphide under study.

The structures of 2-*n*-butylthiolane and 2-*n*-propylthiacyclohexane can be readily deduced from their mass spectra (Fig. 7(a) and (b)) since the base ions in both spectra are due to the loss of the substituent from the α-carbon atom. In the case of the

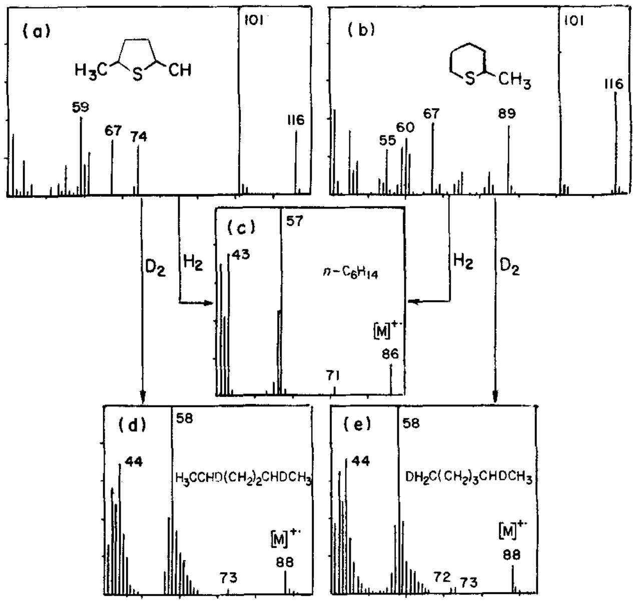

Figure 4. The mass spectra of (a) 2,5-dimethylthiolane, (b) 2-methylthiacyclohexane, (c) *n*-hexane, (d) 2,5-dideuteriohexane and (e) 1,5-dideuteriohexane.

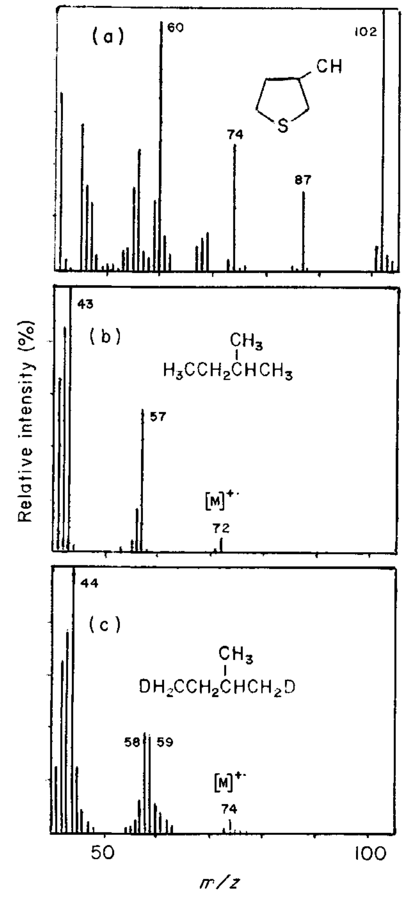

Figure 5. The mass spectra of (a) 3-methylthiolane, (b) 2-methylbutane and (c) 1,4-dideuterio-2-methylbutane.

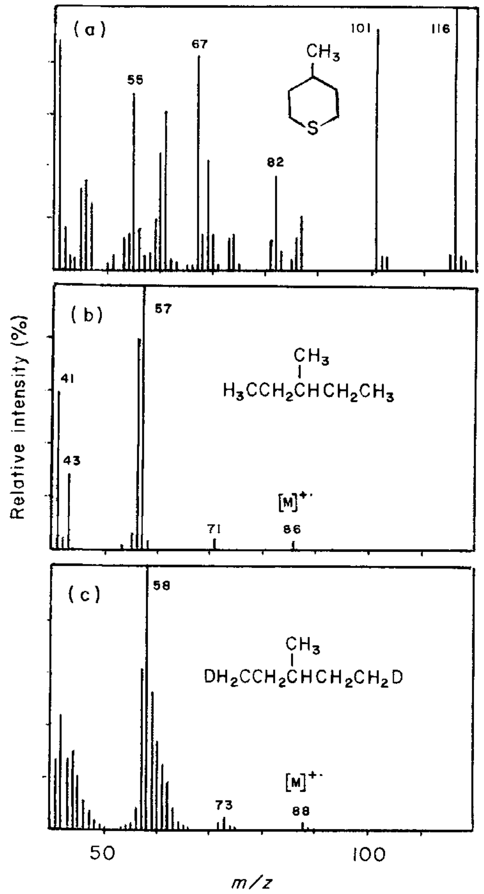

Figure 6. The mass spectra of (a) 4-methylthiacyclohexane, (b) 3-methylpentane and (c) 1,5-dideuterio-3-methylpentane.

latter compound, however, there are other possible structures which would satisfy the spectrum, namely, 2-*n*-propyl-3(4,5)-methylthiolanes. Since hydrodesulphurization of this compound leads to *n*-octane (Fig. 7(c)), the sulphide cannot contain substituents at positions 3 and 4. Also, the presence of the doublet corresponding to the $[M-C_2H_5]^+$ and $[M-C_2H_4D]^+$ ions in the spectrum of the labelled derivative (Fig. 7(d)) indicates that the deuteriated hydrocarbon is 1,5-dideuteriooctane and, hence, that the original sulphide was 2-*n*-propylthiacyclohexane. The presence of the $[M-C_2H_5]^+$, $[M-C_2H_4D]^+$ and $[M-C_3H_7]^+$ and $[M-C_3H_6D]^+$ ions in the spectrum of the deuteriated hydrocarbon (Fig. 7(e)) obtained from 2-*n*-butylthiolane is as expected for that sulphide.

It was mentioned earlier[4] that the fragmentation mode of 3-alkylthiacyclohexane resembles closely that of the 2-alkyl isomers, which is due to ease of elimination of substituents from the molecular ions in both cases. This is exemplified by the spectrum of 2-*n*-propylthiacyclohexane (Fig. 7(b)) and 3-*n*-butylthiacyclohexane (Fig. 8(a)). At the same time, the fact that the hydrodesulphurization of the latter sulphide gives rise to 4-methyloctane (Fig. 8(b)) and that the mass spectrum registered after deuteriodesulphurization (Fig. 8(c)) contains the $[M-CH_2D]^+$ and $[M-C_3H_6D]^+$ ions satisfies the structure of the sulphide, although 2-methyl-4-*n*-butylthiolane cannot be excluded from consideration.

CONCLUSIONS

The above examples illustrate the great potential of the developed method when structure elucidation of cyclic sulphides is to be made. The greatest accuracy is achieved if combined analysis is made of the mass spectra of the orginal sulphides and hydrocarbons and

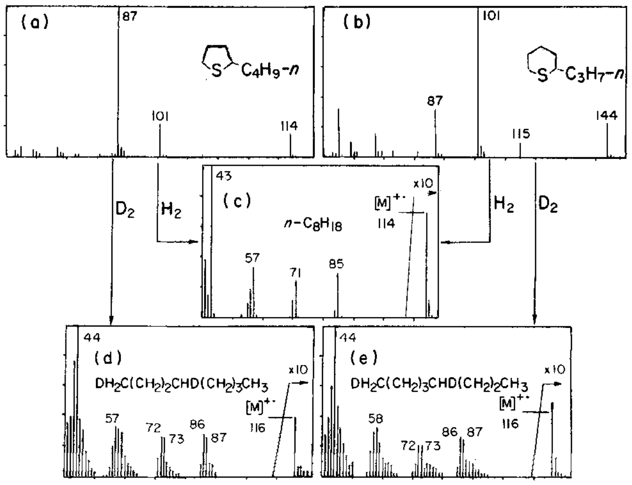

Figure 7. The mass spectra of (a) 2-*n*-butylthiolane, (b) 2-*n*-propylthiacyclohexane, (c) *n*-octane, (d) 1,4-dideuteriooctane and (e) 1,5-dideuteriooctane.

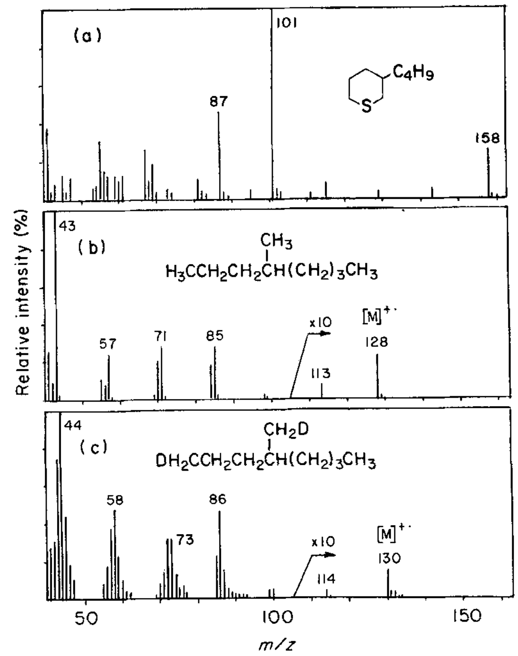

Figure 8. The mass spectra of (a) 3-*n*-butylthiacyclohexane, (b) 4-methyloctane and (c) 1-deuterio-4-deuteriomethyloctane.

the deuteriated hydrocarbons derived from the sulphides. It should be noted that the method does not permit the differentiation of stereoisomers.

The method is also applicable to polycyclic sulphides. The use of deuterium in this case is, however, frequently inefficient, since the determination of the position of label in alkylcycloalkanes (or polycyclanes) produced under deuteriodesulphurization conditions is not always possible.

The method can also be used for the structure investigation of individual sulphides. In this case, the chromatographic column may be excluded and the injection port may be connected directly with the molecular separator by using the tube.

EXPERIMENTAL

The mass spectra of the compounds studied have been described previously.[4] The desulphurization catalyst was prepared by the method described in Ref. 6 with the exception that Chromaton W (120 mesh) was used as the solid support instead of porous glass.

The work was performed on an LKB-2091 gas chromatograph/mass spectrometer. The mass spectra were registered at ionizing energy 70 eV and emission current 25 μA and the temperature of the ionization chamber was 200 °C. A chromatographic column (3 m × 3 mm) containing 10% ethylene glycole adipate coated on 150 mesh Spherochrom was used.

REFERENCES

1. A. I. Mikaya, L. P. Medvedkova, V. G. Zaikin, V. M. Vdovin and A. A. Kamishova, *Isv. Akad. Nauk SSSR, Ser. Khim.* 1181 (1983).
2. A. I. Mikaya, V. I. Smetanin and V. G. Zaikin, *Izv. Akad. Nauk SSSR, Ser. Khim.* 2214 (1982).
3. A. I. Mikaya , V. I. Smetanin, V. G. Zaikin, A. V. Antonova and N. S. Prostakov, *Org. Mass Spectrom.* **18**, 99 (1983).
4. V. G. Zaikin, E. A. Trusova and L. P. Stcherbakova, *Khim. Geterotsikl. Soedin.* 176 (1978).
5. G. J. Thompson, H. J. Coleman, C. C. Ward and H. T. Rall, *Anal. Chem.* **32**, 424 (1960).
6. J. Undeova and J. Janek, *J. Chromatogr.* **65**, 179 (1972).

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