

IDENTIFICATION OF NATURALLY OCCURRING CYCLIC SULFIDES IN A WILMINGTON, CALIF., CRUDE OIL DISTILLATE BOILING FROM 111° TO 150° BY USE OF A SERIES OF GAS-LIQUID CHROMATOGRAPHY STATIONARY PHASES

H. J. COLEMAN, C. J. THOMPSON, R. L. HOPKINS AND H. T. RALL

Bartlesville Petroleum Research Center, Bureau of Mines, U.S. Department of the Interior, Bartlesville, Okla. (U.S.A.)

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INTRODUCTION

Knowledge of the natural occurrence of sulfur compounds in petroleum is important and useful not only in processing applications, but also in fundamental studies related to the composition and origin of petroleum. Information as to the type of sulfur compounds in petroleum is likewise important. Although the authors have isolated and identified many individual sulfur compounds of various types in selected crude oils¹⁻⁶, this paper is concerned only with the cyclic sulfide type in Wilmington, Calif., crude oil.

The development of gas-liquid chromatographic (GLC) techniques in recent years constitutes a major technological advance in the analysis of complex cyclic sulfide containing fractions. An analysis of fractions trapped directly from GLC columns, by mass and infrared spectroscopy and by the newer technique of hydrogenolysis⁷, combined with the knowledge of the GLC retention time of the trapped fraction and of its components, provides a basis for the complete resolution and identification of individual constituents of very complex mixtures. This paper describes the firm identification of 18 cyclic sulfides in a Wilmington, Calif., crude oil distillate, having a boiling range of 111° to 150°, by using the techniques mentioned and also discusses the systematic liquid-solid and gas-liquid chromatographic procedures used in concentrating and isolating each individual cyclic sulfur compound.

REVIEW OF PREVIOUS WORK

Historically, as early as 1900, MABERY AND QUAYLE⁸ mentioned the possible presence of cyclic sulfides as a class in petroleum. Six years later, these researchers⁹, although not identifying any specific compound, did isolate from a sulfuric acid extract of a Canadian petroleum several compounds of the general formula $C_nH_{2n}S$ which they designated as thiophanes. Sulphuric acid extracts from petroleum fractions served as the source materials in later cyclic sulfide identification studies as those reported by THIERRY¹⁰, in 1925, on an Iranian crude oil; CHALLENGER¹¹, in 1926, on a Kimmeridge shale oil; MCKITTRICK¹², in 1929, on a cracked naphtha of a California crude oil; and many others¹³⁻²⁰ through 1955.

O. L. POLLY, in a paper published in 1942²¹, described cyclic sulfide separation from a California (Santa Maria Valley) straight-run gasoline using aluminum chloride extraction. Other researchers^{22,23} reported the isolation of cyclic sulfides by mercuric chloride extraction. More recent investigators^{24,25} have used a distillation step for securing distinct boiling range distillates, followed by concentration of the sulfur compounds by adsorption chromatography on silica or alumina gel. Extraction by chemical methods either before²⁶ or after²⁷ liquid-solid chromatography has been reported as advantageous in achieving otherwise difficult sulfur compound type separations.

After isolating cyclic sulfides as a class from petroleum, early researchers found the actual isolation of the individual cyclic sulfides and their firm identification difficult. This problem is understandable because of lack, at that time, of adequate equipment and analytical methods and the almost complete dependence for identification upon elemental analysis and melting point determinations of chemical derivatives. Because of the presence of so many close-boiling isomers, including stereoisomers, many of these early investigations were not specific enough to establish individual identifications except for a few simple sulfides. In addition, sample treatment in much of the early work was conducive to thermal or chemical degradation. Continual improvement of separation techniques^{15,24} combined with the development of analytical methods such as Raney nickel desulfurization²⁰ and infrared spectral comparisons^{20,28} has provided simpler procedures and firmer bases for individual sulfur compound identifications. In addition, the recent availability of increased numbers of reference standards has aided cyclic sulfide identifications. British Petroleum Co. chemists²⁰ reported in 1951 the synthesis of several cyclic sulfides, including the individual *cis* and *trans* isomers of 2,5-dimethylthiacyclopentane. In 1962, YUR'EV³⁰ published a comprehensive review on cyclic sulfide syntheses, which included his own work dating as far back as 1937, as well as that of many others.

Numerous cyclic sulfide syntheses within our own laboratory, some of which are reported by HOPKINS^{31,32}, provided reference compounds for the experimental work reported below.

EXPERIMENTAL

Preparation of sulfur-compound concentrate

The separation and identification of individual sulfur compounds from a crude oil represent a difficult and oftentimes tedious problem because only minute quantities are usually present. The processing steps used in concentrating the cyclic sulfides from Wilmington, Calif., crude oil included isothermal distillation, fractional distillation at reduced pressure, and liquid-solid chromatography.

Isothermal distillation. Isothermal distillation was the initial step of a sequence of processing steps used to secure a suitable straight-run distillate from 165.37 kg (approx. 50 gals.) of Wilmington, Calif., crude oil. The isothermal distillation treatment consisted first of passing the crude oil through an all-glass, 100° steam heated, falling-film flash still at a rate of 30-40 ml/min against a countercurrent helium sweep of 9 l/min. The initial crude oil pass at atmospheric pressure produced a distillate complete through 111°. The residue was passed through the isothermal still at 100 mm Hg pressure to remove all distillate boiling below 150°. This procedure,

which employs a sample contact time of less than 30 sec and a temperature never exceeding 100°, minimized the possibility of thermal degradation. A paper by H. T. RALL *et al.*³³ gives a working drawing of the isothermal still and describes in detail the apparatus and its operation.

Vacuum fractionation. Fractionation of the distillate recovered from the isothermal still into definite boiling ranges limits the molecular weight spread of the fractions to be studied. The "111° to 150°" boiling range designation for the distillate investigated is not exact because of limitations of vacuum fractionation and of azeotropic effects³⁴. However, the use of reduced pressure during fractionation in an all-glass Oldershaw column avoided exposing distillate samples to temperatures in excess of 100°, and possible thermal degradation during sample handling. The 111° to 150° boiling range sample, denoted by the top rectangle of Fig. 1, comprised 2.70% of the original crude oil and contained only 0.038% sulfur. Although not necessary for an understanding of the analyses discussed in this paper, Fig. 1 of ref. 6 outlines the processing measures that produced this 111° to 150° boiling range distillate.

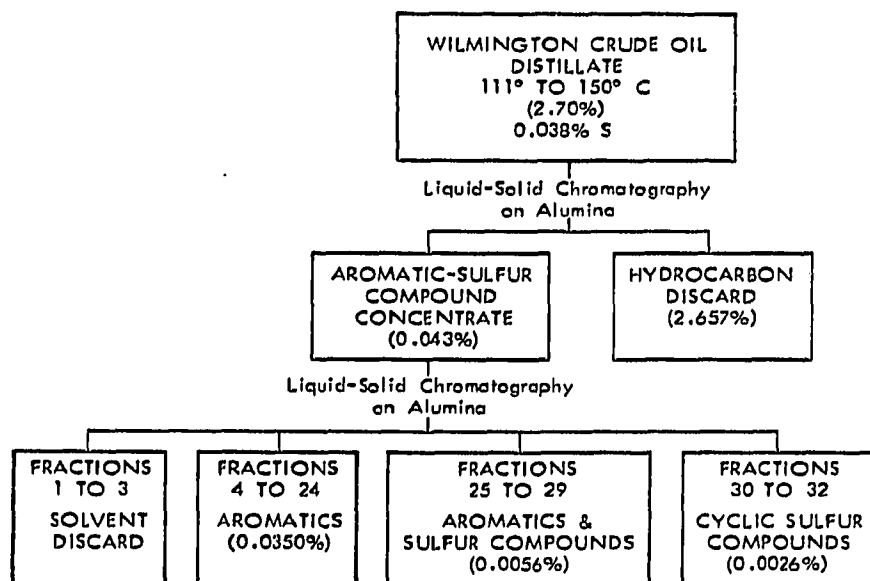


Fig. 1. Outline of distillate treatment used in producing sulfur-compound concentrates.

Liquid-solid chromatography. Liquid-solid chromatography on either silica gel or alumina gel concentrates organic compounds by type, and the previous section cites the work of some earlier researchers who used silica gel for their sulfur compound concentrations. However, the authors' experience indicated that alumina gel accomplishes a better resolution between aromatics and sulfur compounds than does silica gel.

The initial liquid-solid chromatographic step, shown in Fig. 1, involved percolating a 2.3 kg portion of the 111° to 150° distillate in four 750 ml batch runs through alumina (Alcoa H-41)*. These preliminary adsorption runs, employing dilution and elution techniques, removed a large amount of the aromatics from the sulfur compounds. The resulting sulfur-compound concentrate constituted the sample charge

* Reference to specific brand names is made to facilitate understanding and does not imply endorsement of such brands by the Bureau of Mines.

in the second liquid-solid chromatographic treatment of Fig. 1. This latter treatment, employing a high efficiency adsorption column (12 mm \times 12.2 m glass column containing 1350 ml of alumina), yielded a number of small (0.7 to 1.5 g) fractions, some of which contained only cyclic sulfides as denoted in the lower right hand block of Fig. 1. Only four adsorption fractions, namely 28, 29, 30 and 31, are considered in the following discussion.

Separation and identification of cyclic sulfides in concentrate fractions

In general, the procedure followed in identifying individual sulfur compounds involved the trapping of material emerging from a GLC unit (as indicated by a "peak" in the chromatogram) and the subsequent analysis of the material trapped. Examination of trapped material by desulfurization⁷ often indicated that two or more compounds were present in the trapped material. Such mixtures required rechromatographing of the trapped material on another GLC column using a stationary phase of differing polarity. Frequently, the compound or compounds suggested by the desulfurization data were not available, necessitating their synthesis as reference materials. The final confirmation of identification of an isolated compound depended on a comparison of its infrared spectrum with that of the reference material.

A Perkin-Elmer Model 154-D Vapor Fractometer, equipped with a thermistor-type thermal detector, produced the chromatograms of the alumina adsorption fractions 28 through 31 shown in Figs. 2 and 4. Although the column operating temperature was reduced slightly to improve the sulfur compound separations, the column and conditions were similar to those of the earlier study⁶, specifically a 1/4 in. \times 40 ft. aluminum tube packed with Reoplex 400 (polypropylene glycol adipate) on a 30-42 mesh GC-22 "Super support" (20/100 wt. ratio) at a temperature of about 117°, and a helium flowrate of 60 ml/min.

Fraction 29, GLC time interval 34 to 39 min. The chromatograms of liquid-solid chromatographic fractions 28 through 31, shown in Fig. 2, indicate striking differences of adsorptive strength on alumina for several sulfur compounds. Some carryover of the alkylthiophenes, as well as of some aromatics (benzene, toluene, and *o*-xylene), into the predominantly cyclic sulfide fraction 29 is indicated by comparison with the chromatogram of fraction 28. The chromatogram of fraction 29 illustrates a unique separation of two sulfur compounds, 2,2,5,5-tetramethylthiacyclopentane and 2,2,5-trimethylthiacyclopentane, on the basis of their selective retention on alumina. These two sulfides, represented by the two attenuated peaks on the chromatogram of fraction 29 at 35 and 38 min respectively, were not present in fraction 28 (indeed no cyclic sulfides were present in fraction 28) and are essentially absent in fraction 30. Thus, alumina adsorption concentrated these two cyclic sulfides almost entirely into fraction 29. GLC separation on the selective polar stationary phase, Reoplex 400, isolated these two compounds in an unusual manner as is evident in the following discussion. Trapping the compounds from the GLC column during the appropriate time interval was readily accomplished. Mass spectrometer analyses of the trapped fractions suggested the presence of two cyclic sulfides of molecular weight 144 for the material producing the peak at 35 min and 130 for the material producing the second peak at 38 min. Desulfurization not only substantiated the fact that a higher molecular weight compound eluted first but also provided a basis for structure assignment in that the trapped material of the first peak, upon desulfurization, produced

2,5-dimethylhexane and that of the second peak produced 2-methylhexane. Following synthesis of a number of cyclic sulfides, whose structures and properties were compatible with known facts, the GLC retention times and infrared spectral data for the two compounds, 2,2,5,5-tetramethylthiacyclopentane and 2,2,5-trimethylthiacyclopentane, were found to agree with those of the two compounds isolated from the petroleum fraction. The early GLC separation of these two highly methylated cyclic sulfides is readily understood from the data of Fig. 3 which shows the relationship of adjusted retention time (retention time minus time of air peak) with carbon number for a series of thiacyclopentanes on Reoplex 400 and on a number of other stationary phases.

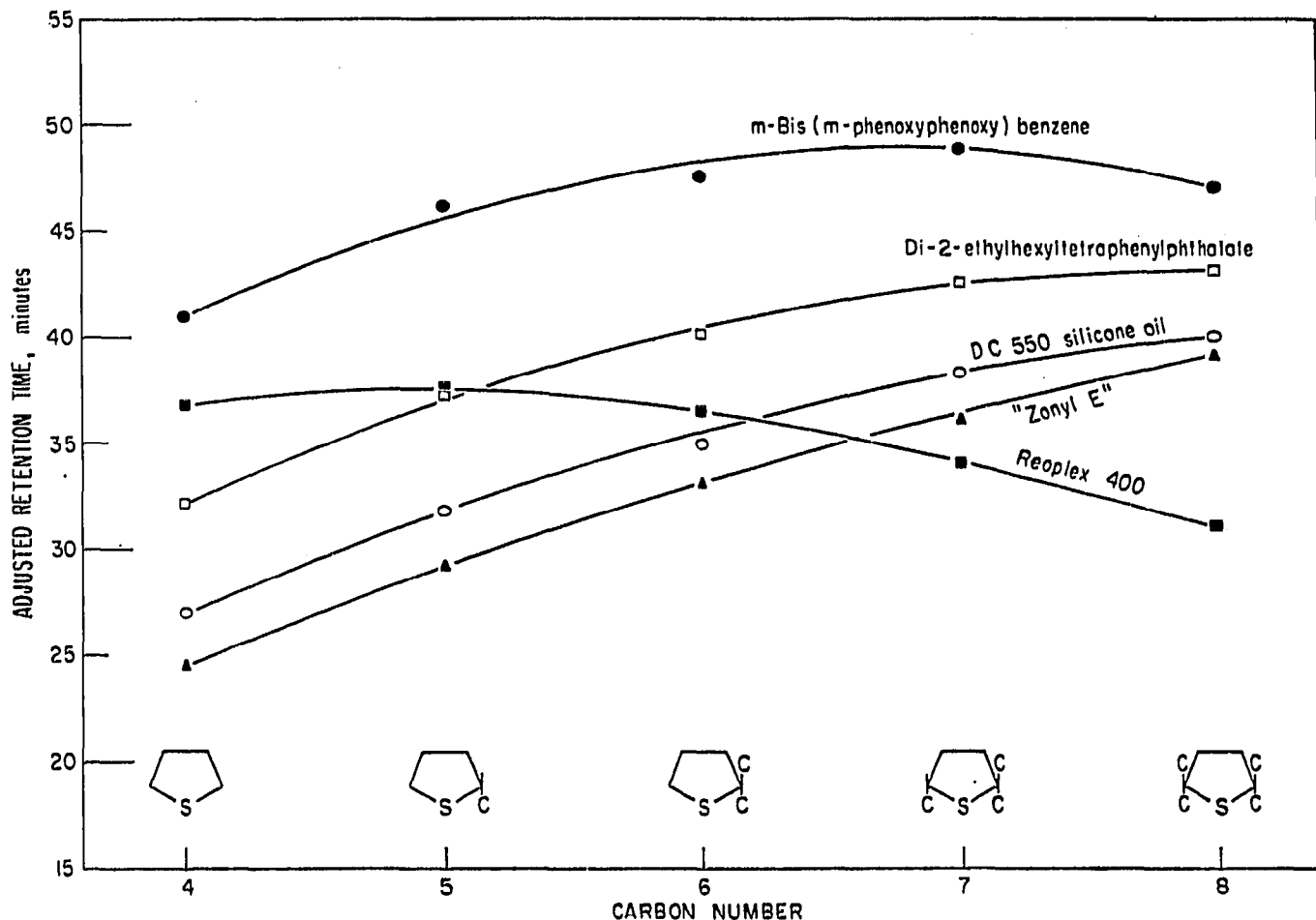


Fig. 3. Retention time relationship for a series of thiacyclopentanes on stationary phases of differing polarity.

Fraction 29, GLC time interval 39 to 43 min. Although known GLC retention times of available sulfides suggest the possibility of several components in the major peak at 40 min, the alumina adsorption separation provided effective simplification so that the material represented by this peak is almost solely *trans*-2,5-dimethylthiacyclopentane. The shoulder on the trailing edge of this peak represents a fairly small quantity of the *cis* isomer. The ratio of the quantity of the two stereoisomers became reversed in fraction 31 and the *cis* isomer predominated by approximately two to one in that fraction. Thus, *trans*-2,5-dimethylthiacyclopentane was separated

and identified from fraction 29 while fraction 31 was used as source material in separating and identifying *cis*-2,5-dimethylthiacyclopentane. 2-Methylthiacyclopentane, a compound of comparable retention time and a possible interference, was adsorbed strongly enough on the alumina that it did not appear until fraction 30 and then only in minor quantity. Therefore, this compound represented no separation problem in fraction 29. 2,2-Dimethylthiacyclopentane, inseparable from *trans*-2,5-dimethylthiacyclopentane on the Reoplex column (and on most other columns tried) was present in both fractions 29 and 30. The only GLC column found that would separate the relatively small quantities of 2,2-dimethylthiacyclopentane from *trans*-2,5-dimethylthiacyclopentane was an 1/4 in. \times 40 ft. "Aroclor 1260" (a chlorinated biphenyl manufactured by Monsanto Chemical Co.) column operating at about 145°. The infrared spectrum of 2,2-dimethylthiacyclopentane, thus isolated and purified, was obtained and found to agree with the spectrum of a reference sample.

Fraction 29, GLC time interval 47 to 52 min. The next two major peaks of fraction 29 at 48.2 and 49.7 min, although agreeing to some extent with the retention time of 2,5-dimethylthiophene and 2-ethylthiophene respectively of fraction 28, actually were produced almost solely by cyclic sulfides. Repeated trapping and rechromatographing on other GLC columns resulted in isolating sufficient material of these two peaks for analysis by both desulfurization and infrared. Lack of reference compounds prevented a firm identification, but desulfurization of the materials of both peaks produced predominantly 3-methylhexane which could have originated from 15 isomers (including *cis-trans* configurations). The availability of 2-methyl-2-ethyl- and the 2-ethyl-3-methylthiacyclopentanes (possible precursors of 3-methylhexane) as reference compounds allowed their elimination from consideration as compounds causing these two peaks. However, most of the other isomers can be eliminated as unlikely precursors of 3-methylhexane in this fraction through knowledge of structure-retention time relationships of known cyclic sulfides. For example, the possible C₇ thiacyclohexanes can be eliminated from consideration by the following reasoning. 2-Methylthiacyclohexane, a C₆ cyclic sulfide having a retention time of 57.4 min, emerges more than 7 min later than the compounds forming the two peaks under discussion. The addition of a methyl group at the required position of the ring would increase the retention time measurably, thus effectively eliminating these compounds from consideration. Similar reasoning applied to the various thiacyclopentanes, leaves only the four stereoisomers of 2,3,5-trimethylthiacyclopentane as possible precursors of the desulfurization product, 3-methylhexane. BIRCH, in 1955¹⁹ cited the identification of 2,3,5-trimethylthiacyclopentane in a crude oil concentrate also on the evidence of 3-methylhexane identified in the product from a Raney nickel desulfurization of the concentrate.

The material of the first peak (48.2 min) produced a small quantity of 2,2-dimethylpentane which could have originated from only two cyclic sulfides, 2,4,4-trimethylthiacyclopentane or 3,3-dimethylthiacyclohexane, discounting thiacyclopropanes and thiacyclobutanes as probable petroleum components. 3,3-Dimethylthiacyclohexane is eliminated from consideration by comparison of its retention time with that of 2,2-dimethylthiacyclohexane. This is because the retention time of 2,2-dimethylthiacyclohexane is much greater than that of the 48.2 min peak and the 3,3-substitution should tend to increase the retention time thus effectively eliminating 3,3-dimethylthiacyclohexane as the precursor. The identification of 2,4,4-trimethyl-

thiacyclopentane therefore is indicated by GLC and desulfurization with little doubt despite the lack of a reference sample.

Without reference compounds, the identification of 2,4,4- and 2,3,5-trimethylthiacyclopentanes are considered tentative, and the compounds are not included in the list of firm identifications for this 111° to 150° boiling range distillate.

Fractions 30 and 31. Except for trace impurities (16–36 min in fraction 31) from the ethanol desorbent, fractions 30 and 31 (Fig. 2) consist only of cyclic sulfides. A comparison of the chromatograms of the two fractions showed further evidences of selective retention on alumina. Thiacyclohexane, for instance, as analyzed with the Reoplex GLC column, was barely perceptible in fraction 30 while appearing as a sizeable component in fraction 31. The same trend is true for the *trans*-3,4-dimethylthiacyclopentane and inspection of the consecutive chromatograms of Fig. 2 show that the *cis* isomer doesn't appear until fraction 31 which provides additional evidence that the *trans*-isomers are less strongly adsorbed on alumina (see discussion on *cis*- and *trans*-2,5-dimethylthiacyclopentane). Although not readily evident from the Reoplex separation, a greater abundance of the *trans* isomers over the *cis* isomers in this particular boiling range distillate is indicated by a comparison of data from other GLC columns.

Techniques used in the identification program—further discussion

Gas-liquid chromatography. Fig. 4 shows the chromatograms of the cyclic sulfide fraction 31 obtained with three different GLC stationary phases. Although a large portion of the compounds identified in this study were resolvable with the Reoplex column (see top panel), no single column could provide all the separations necessary for isolating each compound to determine quantitative relationships and to confirm identification by infrared spectrometry. The resolution of fraction 31, obtained with the di-2-ethylhexyltetraphenylphthalate* GLC column shown in the center panel, appears to be poor except for the excellent isolation achieved for the 2-methylthiacyclopentane at 41 minutes and of *trans*-2,4-dimethylthiacyclopentane at 50 min. However, the order of elution of isomers on this column was so different from those on Reoplex that, in many instances, material could be trapped from one column and rechromatographed on the other to effect good resolution of the individual components. The opportunity for complete resolution of each individual compound by this technique is made even more evident by considering the resolution obtained with the *m*-bis(*m*-phenoxyphenoxy)benzene column as shown in the bottom panel. This latter column is the only one of the three (as well as of many others tested) that clearly isolated the 3-methylthiacyclopentane as a single "peak". It also produced the best separation of *cis*- and *trans*-dimethylthiacyclopentane. Thus, trapping the material of the major peak emerging from 39 to 43 min from the Reoplex column and rechromatographing on the phthalate column resolved the theoretically four component mixture into two distinct peaks. The material of the first peak consisted solely of 2-methylthiacyclopentane and that of the second peak only *cis*- and *trans*-2,5-dimethylthiacyclopentane. The 2,2-dimethyl isomer, a possible contaminant because of its retention time, (retention time indicated in Fig. 4) had been eluted in the earlier fractions 29, and 30 and was not present in fraction 31. Trapping of the

* A stationary phase synthesized in our laboratory.

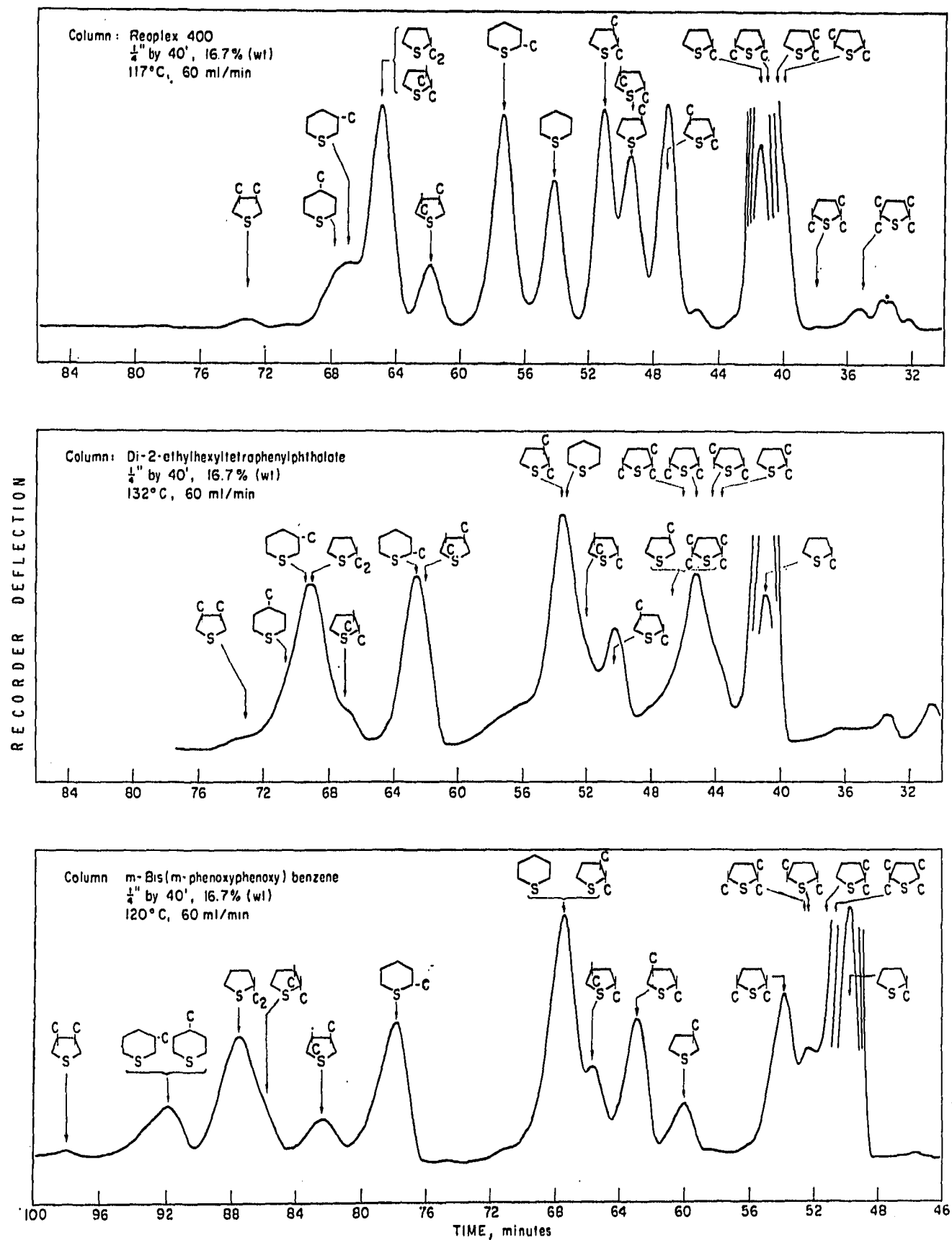


Fig. 4. Gas-liquid chromatograms showing resolution of cyclic sulfides in fraction 31 achieved with various GLC stationary phases.

material emerging as the second peak from the phthalate column rerun of trapped material from the Reoplex column and rechromatographing it in the phenoxyphenoxy benzene column resulted in resolving the individual *cis*- and *trans*-2,5-dimethylcyclopentanes into two distinct peaks for further qualitative tests. The same technique was applied to the separation of other mixtures from the Reoplex column as: 3-methylthiacyclopentane and the *cis*-2,4-dimethylthiacyclopentane which emerged at 49.5 minutes, and 2-ethylthiacyclopentane and *cis*-2,3-dimethylthiacyclopentane which emerged at 65.0 min.

Microdesulfurization. Microdesulfurization of GLC fractions constitutes a recent important development in the art of structure characterization⁷. An example of the efficacy of desulfurization was discussed earlier in the text, and this technique was employed in all the cyclic sulfide identifications in which it provided important structure information. Desulfurization alone cannot always define the structure of a precursor completely. A given hydrocarbon may be derived from two or more sulfides, any or all of which may be present in a given mixture, *e.g.* 2-methylthiacyclohexane, 2-ethylthiacyclopentane, and *cis*- and *trans*-2,5-dimethylthiacyclopentane all produce *n*-hexane. However, the hydrocarbon resulting from desulfurization does point effectively to the possible presence of certain molecules and to the rejection of others. This evaluation allows selection of proper compounds to check for agreement with respect to retention times and for infrared and/or mass spectra determination.

Infrared spectroscopy. Final proof of identification of all cyclic sulfides listed in Table I consisted of comparing the infrared spectrum of a reference compound with that of the isolated material trapped as effluent from a GLC column. Spectra were determined on a Perkin-Elmer Model 21 spectrophotometer using a Barnes Engineering Co. Type "D" ultra-micro cavity cell of 0.05 mm path length and a Perkin-Elmer 4 \times beam condenser.

The authors include only two examples of the spectral comparisons obtained in this study for confirming the identification of each of the cyclic sulfides found in this

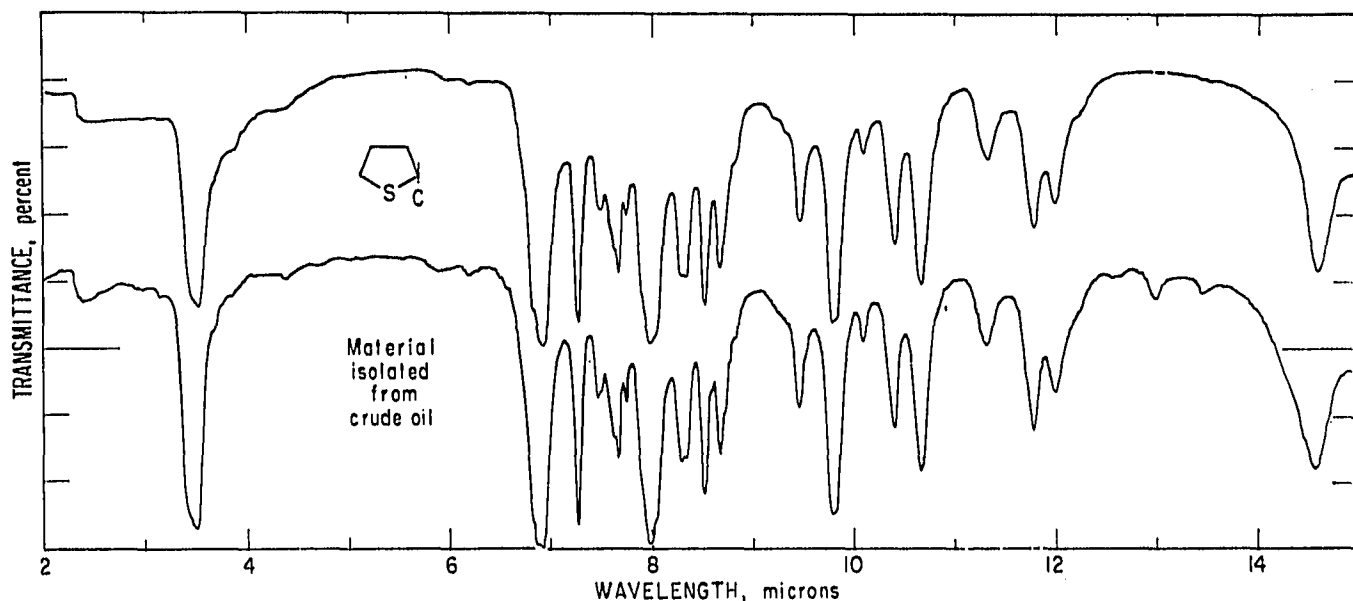


Fig. 5. Comparison of infrared spectrum of 2-methylthiacyclopentane with spectrum of material isolated from Wilmington, Calif., crude oil.

TABLE I

CYCLIC SULFIDES IDENTIFIED IN WILMINGTON, CALIFORNIA, DISTILLATE BOILING 111° TO 150°

Name	Structural formula	
$C_6H_{10}S$		
2-Methylthiacyclopentane		
3-Methylthiacyclopentane		
Thiacyclohexane		
$C_8H_{12}S$		
2,2-Dimethylthiacyclopentane		
<u>cis</u> -2,3-Dimethylthiacyclopentane		
<u>trans</u> -2,3-Dimethylthiacyclopentane		
<u>cis</u> -2,4-Dimethylthiacyclopentane		
<u>trans</u> -2,4-Dimethylthiacyclopentane		
<u>cis</u> -3,4-Dimethylthiacyclopentane		
<u>trans</u> -3,4-Dimethylthiacyclopentane		
<u>cis</u> -2,5-Dimethylthiacyclopentane		
<u>trans</u> -2,5-Dimethylthiacyclopentane		
2-Ethylthiacyclopentane		
2-Methylthiacyclohexane		
3-Methylthiacyclohexane		
4-Methylthiacyclohexane		
$C_9H_{14}S$		
2,2,5-Trimethylthiacyclopentane		
$C_8H_{18}S$		
2,2,5,5-Tetramethylthiacyclopentane		

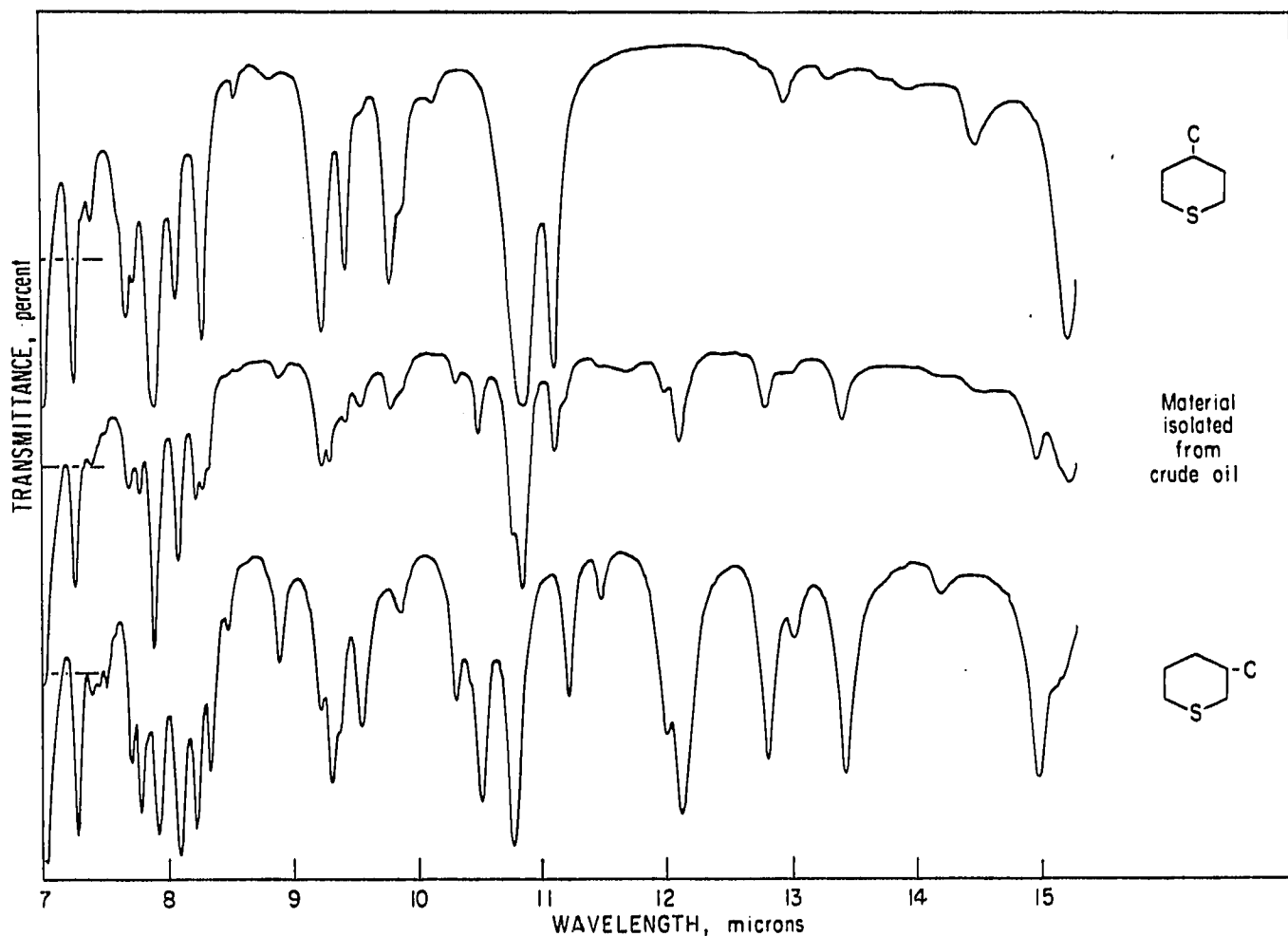


Fig. 6. Comparison of infrared spectra of 4-methylthiacyclohexane and 3-methylthiacyclohexane with spectrum of material isolated from Wilmington, Calif., crude oil.

boiling range distillate. Fig. 5 shows a comparison of the infrared spectrum of reference 2-methylthiacyclopentane with the infrared spectrum of material isolated from fraction 31. Except for three minor absorption bands in the 12.5 to 13.5 micron range the spectra are identical; the spurious bands are those of an impurity in the sample. Fig. 6 shows a comparison of the infrared spectra of 4-methylthiacyclohexane (at the top of the figure) and 3-methylthiacyclohexane (at the bottom of the figure) compared with the infrared spectrum of material collected from the GLC column. In this instance, because 3- and 4-methylthiacyclohexanes were inseparable by GLC columns used in this investigation, they were analyzed as a mixture. In some instances, extra sample handling reduced sample size to the extent that a slight amount of carbon disulfide solvent was necessary to wash the sample from the trap into the infrared cell. Thus, the spectrogram scan in Fig. 6 starts at seven microns to omit the large carbon disulfide absorption band. The excellent agreement of the reference spectra with the cyclic sulfide material isolated from the Wilmington 111° to 150° distillate in both Figs. 5 and 6 confirms identification of the sulfur compounds. Other cyclic sulfides were similarly identified and are included in the list of 18, positively identified, cyclic sulfides of Table I.

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SUMMARY

This paper describes the positive identification of 18 cyclic sulfides in a Wilmington, Calif., 111° to 150° distillate. The systematic procedures employed for separating and identifying the cyclic sulfides included isothermal distillation, vacuum fractionation, liquid-solid chromatography (alumina adsorption), gas-liquid chromatography, microdesulfurization, and infrared spectrometry. The isolation of each individual cyclic sulfide required the use of more than one GLC stationary phase. Final identification of isolated sulfides was established by infrared spectral comparisons with reference compounds.

REFERENCES

- 1 H. J. COLEMAN, C. J. THOMPSON, R. L. HOPKINS, N. G. FOSTER, M. L. WHISMAN AND D. M. RICHARDSON, *J. Chem. Eng. Data*, 6 (1961) 464.
- 2 C. J. THOMPSON, H. J. COLEMAN, R. L. HOPKINS AND H. T. RALL, *J. Chem. Eng. Data*, 9 (1964) 293.
- 3 C. J. THOMPSON, H. J. COLEMAN, R. L. HOPKINS AND H. T. RALL, *J. Chem. Eng. Data*, 9 (1964) 473.
- 4 H. J. COLEMAN, C. J. THOMPSON, R. L. HOPKINS AND H. T. RALL, *J. Chem. Eng. Data*, 10 (1965) 80.
- 5 C. J. THOMPSON, H. J. COLEMAN, R. L. HOPKINS AND H. T. RALL, *J. Chem. Eng. Data*, 10 (1965) 279.
- 6 H. J. COLEMAN, C. J. THOMPSON, R. L. HOPKINS AND H. T. RALL, *J. Chromatog.*, 20 (1965) 240.
- 7 C. J. THOMPSON, H. J. COLEMAN, C. C. WARD AND H. T. RALL, *Anal. Chem.*, 32 (1960) 424.
- 8 C. F. MABERY AND W. O. QUAYLE, *J. Soc. Chem. Ind.*, 19 (1900) 505.
- 9 C. F. MABERY AND W. O. QUAYLE, *Am. Chem. J.*, 35 (1906) 404.
- 10 E. H. THIERRY, *J. Chem. Soc.*, (1925) 2756.
- 11 F. CHALLENGER, J. HASLAM, R. J. BRAMHALL AND J. WALKDEN, *J. Inst. Petrol.*, 12 (1926) 106.
- 12 D. S. MCKITTRICK, *Ind. Eng. Chem.*, 21 (1929) 585.
- 13 W. FRIEDMAN AND C. CANSECO, *Petrol. Refiner*, 22 (1943) 1.
- 14 W. FRIEDMAN AND C. RODRIGUEZ, *Petrol. Refiner*, 25 (1946) 53.
- 15 D. HARESNAP, F. A. FIDLER AND R. A. LOWRY, *Ind. Eng. Chem.*, 41 (1949) 2691.
- 16 S. F. BIRCH AND D. T. McALLAN, *J. Inst. Petrol.*, 37 (1951) 443.
- 17 R. H. BROWN AND S. MEYERSON, *Ind. Eng. Chem.*, 44 (1952) 2620.
- 18 S. F. BIRCH, *J. Inst. Petrol.*, 39 (1953) 185.
- 19 R. EMMOTT, *J. Inst. Petrol.*, 39 (1953) 695.
- 20 S. F. BIRCH, T. V. CULLUM, R. A. DEAN AND R. L. DENYER, *Ind. Eng. Chem.*, 47 (1955) 240.
- 21 O. L. POLLY, A. C. BYRNS AND W. E. BRADLEY, *Ind. Eng. Chem.*, 34 (1942) 755.
- 22 I. TEUTSCH, *Petrol. Z.*, 30 (1934) 1.
- 23 S. S. NAMETKIN AND A. S. SOSNINA, *Dokl. Akad. Nauk SSSR*, 63 (1948) 391.
- 24 C. J. THOMPSON, H. J. COLEMAN, H. T. RALL AND H. M. SMITH, *Anal. Chem.*, 27 (1955) 175.
- 25 S. L. GUSINSKAYA, in *Chemistry of Organic Sulfur Compounds in Petroleum and Petroleum Products*, (*Khimiya Serya-Organicheskikh Soedinenii, Soderzhashchikhsya v Neft'yakh i Nefteproduktakh*), *Proc. 3rd Sci. Session, Ufa, 1957*, Israel Program for Scientific Translations, Jerusalem, Vol. 2, 1965, pp. 73-76 (available from the Office of Technical Services, U.S. Dept. of Commerce, Washington, D.C. 20240).
- 26 E. N. KARAULOVA, G. D. GALPERN AND B. A. SMIRNOV, *Tetrahedron*, 18 (1962) 1115.

- 27 R. L. HOPKINS, H. J. COLEMAN, C. J. THOMPSON AND H. T. RALL, *Extraction of Sulfides from Petroleum Fractions by Conversion to Sulfonium Salts*, U.S. Bur. Mines Rept. Invest. 6458, 1964, 20 pp.
- 28 H. J. COLEMAN, C. J. THOMPSON, R. L. HOPKINS AND H. T. RALL, *Identification of Sulfur Compounds in Petroleum—Analysis of a Wasson, Texas, Crude Oil Distillate Boiling from 111° to 150°C*, U.S. Bur. Mines Rept. Invest., 6803 (1966) 20 pp.
- 29 E. V. WHITEHEAD, R. A. DEAN AND F. A. FIDLER, *J. Am. Chem. Soc.*, 73 (1951) 3632.
- 30 YU. K. YUR'EV AND E. G. ROZANTSEV, *Russ. Chem. Rev.*, 31 (1962) 87.
- 31 R. L. HOPKINS, H. T. RALL AND R. W. HIGGINS, *131st Meeting, ACS, Miami, Fla., April 7-12, 1957*, Petrol. Div. Preprint, p. 231.
- 32 R. L. HOPKINS, R. W. HIGGINS, H. J. COLEMAN, C. J. THOMPSON AND H. T. RALL, *Synthesis of Cyclic Sulfides*, U.S. Bur. Mines Rept. Invest., (1967) in press.
- 33 H. T. RALL, R. L. HOPKINS, C. J. THOMPSON AND H. J. COLEMAN, *Proc. Am. Petrol. Inst.*, Sect. VIII, 42 (1962) 46.
- 34 D. H. DESTY AND F. A. FIDLER, *Ind. Eng. Chem.*, 43 (1951) 905.

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