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APPLICATION OF METHYLENE INSERTION REACTIONS TO DIALKYL SULPHIDES (C_2H_6S THROUGH $C_6H_{14}S$) TO PRODUCE REFERENCE COMPOUNDS FOR GAS CHROMATOGRAPHY

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SUMMARY

Methylene insertion reactions on dialkyl sulphides in order to produce a mixture of standard compounds for the analysis of isomeric thiaalkanes by gas-liquid chromatography with capillary columns have been studied. Retention indices were determined for 47 dialkyl sulphides produced at 100° on tricresyl phosphate as the stationary phase.

INTRODUCTION

Free radical photochemical methylene insertion reactions have been used effectively for analyzing alkanes and cyclanes by gas-liquid chromatography (GLC)¹⁻⁴. It has been shown⁵ that the methylene insertion reactions of thiophane and thiacyclohexane proceed in a similar manner to the corresponding reactions of cyclopentane and cyclohexane. However, no quantitative characteristics of the reaction have been given that would enable the effect of the sulphur atom to be evaluated. From numerous reported results, it can be assumed that the C-H bonds adjacent to the sulphur atom will differ from the remainder of the C-H bonds in their reactivity towards diazomethane. This effect should result in a distribution of isomers produced by methylene insertion reactions of sulphides different from that observed for the corresponding saturated hydrocarbons.

It is of considerable interest to use the methylene insertion reactions of sulphides in order to produce a large number of thiaalkanes that are otherwise difficult to obtain, and to characterize chromatographically the structure of the sulphides being studied, particularly in connection with the development of chromatographic procedures for analyzing sulphur-containing gasolines.

This paper presents an approximate quantitative characteristic of the deviation in the distribution of dialkyl sulphides and its relationship to the structural characteristics of thiaalkanes.

EXPERIMENTAL

Synthesis of dialkyl sulphides using standard procedures

The symmetrical thiaalkanes used as starting compounds were produced by the reaction of alkyl halides with sodium sulphide. Methyl *tert.*-butyl sulphide was

produced from *tert.*-butyl chloride and methylmagnesium iodide by the Grignard reaction. Ethyl isopropyl sulphide and methyl, ethyl, *n*-propyl and isopropyl *sec.*-butyl sulphides were produced by alkylation of the corresponding mercaptans.

Purification of dialkyl sulphides

Following the conventional purification procedures (washing, drying, distillation), all of the compounds were purified chromatographically by using a PAKhV-05 preparative chromatograph (Institute of Petrochemical Synthesis of the U.S.S.R. Academy of Sciences, Moscow, U.S.S.R.). The column was made of stainless steel with a total length of 9 m, consisting of portions of length 2 m (I.D. 25 mm), 4 m (I.D. 15 mm), 2 m (I.D. 8 mm) and 1 m (I.D. 4 mm). The stationary phase was 15% Apiezon L on INZ-600 brick (0.30–0.65 mm), the carrier gas was helium, the temperature was 100–170°, depending on the boiling point of the sulphide, the detector used was a katharometer and the volume of the sample varied from 0.7 to 1 ml.

Identification of sulphides

The sulphides were identified by adding to the sample for chromatography individual compounds of known structure. Methylene insertion reactions of isomeric sulphides of the same mass give rise to products ("methylenates") that contain sulphides of the same structure. For such components, the structures were confirmed by analyzing mixtures of the corresponding "methylenates" with respect to the relative increase in the peaks common to the chromatograms of these "methylenates". Methyl isobutyl sulphide, methyl *sec.*-butyl sulphide, ethyl isopropyl sulphide and methyl *n*-pentyl sulphide were subjected to chromatographic hydrodesulphurization. A micro-reactor containing 3% of platinum on INZ-600 brick (0.15–0.25 mm) was incorporated into the gas section of a Tsvet-101 chromatograph; the temperature of the reactor was 275°. The length of the capillary copper column was 150 m, with I.D. 0.25 mm. The conditions used were: stationary phase, squalane; carrier gas, hydrogen; feed-rate, 1.2 ml/min; column temperature, 50°; volume of sample, 0.1 μ l; flame ionization detector.

Hydrodesulphurization of the above four dialkyl sulphides gave rise to the following compounds: methane and isobutane; methane and *n*-butane; ethane and propane; and methane and *n*-pentane.

Methylene insertion reactions on dialkyl sulphides

A 40% solution of potassium hydroxide containing N-nitroso-N-methylcarbamide (0.01 g), generated diazomethane, and the dialkyl sulphide being studied (0.1–0.4 ml) was placed in a 1-ml quartz test-tube with a thin jacket for water cooling. Irradiation was carried out with a PRK-2 quartz lamp placed 13 cm from the test-tube; the reaction time was 1.5–3 h. After the end of this photochemical methylene insertion reaction (disappearance of the yellow coloration), the same amount of N-nitroso-N-methylcarbamide was added to the test-tube and the methylene insertion reaction with diazomethane was repeated.

Analysis of "methylenates"

The analysis was carried out by using a Tsvet-101 chromatograph. The length of the stainless-steel capillary column was 50 m, with I.D. 0.25 mm. The conditions

used were: stationary phase, tricresyl phosphate; carrier gas, hydrogen; feed-rate, 1.2 ml/min; column temperature, 100°; volume of sample, 6–8 μ l; flame ionization detector.

RESULTS

Methylene insertion reactions of 18 dialkyl sulphides gave rise to about 50 individual thiaalkanes and their retention indices, I^* , were determined⁶. Table I gives

TABLE I
LOGARITHMS OF REDUCED RETENTION TIME (t'_{R_x}) AND RETENTION INDICES (I)
FOR DIALKYL SULPHIDES ON TRICRESYL PHOSPHATE AT 100°

Formula	Dialkyl sulphide	Log t'_{R_x}	I
C ₂ H ₆ S	C-S-C	1.0792	534
C ₃ H ₈ S	C-S-C-C	1.1761	576
C ₄ H ₁₀ S	C-S-C-C	1.2430	608
C ₅ H ₁₂ S	C C-C-S-C-C	1.2900	640
	C C-S-C-C-C	1.3222	661
	C C-S-C-C-C	1.3892	704
C ₆ H ₁₄ S	C C-S-C-C	1.3962	706
	C C-C-S-C-C	1.4065	712
	C C-S-C-C-C	1.4099	714
C ₆ H ₁₄ S	C C-C-S-C-C	1.4281	723
C ₅ H ₁₂ S	C C C-C-S-C-C-C	1.4314	724
C ₆ H ₁₄ S	C C-C-S-C-C	1.4472	732
C ₆ H ₁₄ S	C C C-S-C-C-C	1.4533	735
	C C		

* $I = [(\log t'_{R_x} - \log t_{R_2}) / (\log t'_{R_{z+1}} - \log t'_{R_2})] + 100z$, where $t'_R = t_R - t_0$, t_0 = retention time of *n*-pentane, t_{R_x} = retention time of tested compound and t_{R_2} and $t_{R_{z+1}}$ = retention times of *n*-alkanes.

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TABLE I (continued)

Formula	Dialkyl sulphide	Log t'_{R_x}	I
	$\begin{array}{c} \text{C} \\ \\ \text{C-S-C-C-C} \end{array}$	1.4625	742
$\text{C}_5\text{H}_{11}\text{S}$	$\begin{array}{c} \text{C} \\ \\ \text{C-S-C-C-C-C} \end{array}$	1.4771	746
$\text{C}_7\text{H}_{16}\text{S}$	$\begin{array}{c} \text{C} \\ \\ \text{C-C-S-C-C} \\ \quad \\ \text{C} \quad \text{C} \end{array}$	1.5729	791
$\text{C}_8\text{H}_{14}\text{S}$	$\begin{array}{c} \text{C} \\ \\ \text{C-C-S-C-C-C} \\ \\ \text{C} \end{array}$	1.5775	794
	$\begin{array}{c} \text{C} \\ \\ \text{C-S-C-C-C-C} \\ \\ \text{C} \end{array}$	1.5798	796
	$\begin{array}{c} \text{C} \\ \\ \text{C-S-C-C-C-C} \\ \\ \text{C} \end{array}$	1.5798	796
	$\begin{array}{c} \text{C} \\ \\ \text{C-S-C-C-C} \\ \\ \text{C} \end{array}$	1.5933	801
	$\begin{array}{c} \text{C-C} \\ \\ \text{C-C-S-C-C-C} \\ \\ \text{C} \end{array}$	1.6107	808
	$\begin{array}{c} \text{C} \\ \\ \text{C-C-S-C-C-C} \\ \\ \text{C} \end{array}$	1.6107	808
	$\begin{array}{c} \text{C} \\ \\ \text{C-S-C-C-C} \\ \\ \text{C} \end{array}$	1.6180	811
	$\begin{array}{c} \text{C} \quad \text{C} \\ \quad \\ \text{C-S-C-C-C-C} \\ \\ \text{C} \end{array}$	1.6253	815
$\text{C}_7\text{H}_{16}\text{S}$	$\begin{array}{c} \text{C} \\ \\ \text{C-C-C-S-C-C} \\ \\ \text{C} \end{array}$	1.6365	820
	$\begin{array}{c} \text{C} \\ \\ \text{C-C-S-C-C-C} \\ \\ \text{C} \end{array}$	1.6484	824
	$\begin{array}{c} \text{C} \quad \text{C} \\ \quad \\ \text{C-C-S-C-C-C} \\ \quad \\ \text{C} \quad \text{C} \end{array}$	1.6580	828
	$\begin{array}{c} \text{C} \\ \\ \text{C-C-S-C-C-C} \\ \\ \text{C} \end{array}$	1.6609	830

TABLE I (continued)

Formula	Dialkyl sulphide	Log t'_{R_s}	I
C ₆ H ₁₄ S	C-C-C-S-C-C-C	1.6812	838
	C-C-S-C-C-C-C	1.6946	844
	C-S-C-C-C-C-C	1.7021	846
C ₇ H ₁₆ S	C-C-S-C-C-C	1.7033	848
	$\begin{array}{c} \quad \\ C \quad C \\ \\ C \end{array}$		
	C-C-S-C-C-C	1.7364	862
	$\begin{array}{c} \\ C \end{array}$		
	C-C-S-C-C-C	1.7404	864
	$\begin{array}{c} \\ C-C \end{array}$		
	C-C-S-C-C-C-C	1.7634	873
	$\begin{array}{c} \\ C \end{array}$		
	C-C-C-S-C-C-C	1.7672	875
	$\begin{array}{c} \\ C \end{array}$		
	C-C-S-C-C-C-C	1.7709	879
	$\begin{array}{c} \\ C \end{array}$		
	C-C-C-S-C-C-C	1.7709	879
	$\begin{array}{c} \\ C \end{array}$		
	C-C-S-C-C-C-C	1.8129	892
	$\begin{array}{c} \\ C \end{array}$		
	C-C-S-C-C-C-C	1.8129	892
	$\begin{array}{c} \\ C \end{array}$		
	C-S-C-C-C-C-C	1.8388	905
	$\begin{array}{c} \\ C \end{array}$		
C-S-C-C-C-C-C	1.8482	908	
$\begin{array}{c} \\ C \end{array}$			
C-S-C-C-C-C-C	1.8603	913	
$\begin{array}{c} \\ C \end{array}$			
C-C-C-S-C-C-C-C	1.8865	923	
C-S-C-C-C-C-C	1.8921	925	
$\begin{array}{c} \\ C \end{array}$			
C-C-S-C-C-C-C-C	1.9165	935	
C-S-C-C-C-C-C-C	1.9243	938	

the logarithms of the retention time and the retention indices for almost all of the dialkyl sulphides that might be present in gasoline fractions. The reproducibility of the retention indices was ± 1 .

The compositions and structures of the compounds studied can be correlated

with the linear dependence of the retention indices on the number of carbon atoms (n) in $C_nH_{2n+2}S$ molecules in homologous series of dialkyl sulphides with various structures. Graphically averaged data for five groups of dialkyl sulphides including some subgroups are represented in Fig. 1. For line 4 the scale of the I axis is shifted upwards by 100 units. The point for dimethyl sulphide ($n = 2$) does not fit on any of the straight lines. Linearity for all subgroups (from various homologous series) was derived using the method of least squares. The correlation factor for all of the straight lines is 0.99 (the results were treated using the least-squares method).

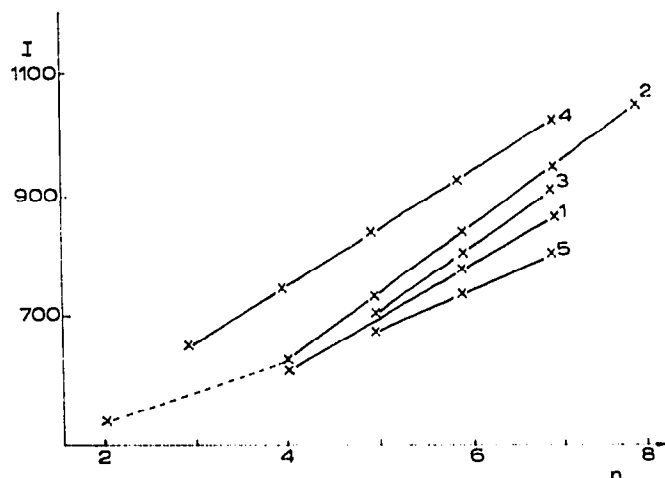


Fig. 1. Relationship between the retention indices (I) and the total number of the carbon atoms (n) in the molecules of dialkyl sulphides for various homologous series on tricresyl phosphate at 100° . 1: (a) $C_m-S-C-C$; (b) $C_m-S-C-C-C$; (c) $C_m-S-C-C-C$; 2: (a) C_m-S-C_m ; (b) $C_m-S-C-C-C$, $m = 1-4$.

3: $C-S-C_m-C-C$; 4: (a) $C-S-C_m$; (b) $C-C-S-C_m$; (c) $C-C-C-S-C_m$, $m = 2-6$. (The scale of the I axis

is shifted upwards by 100 units for this line.) 5: $C_m-S-C-C$, $m = 1-3$.

Table II illustrates the results for three of the eighteen dialkyl sulphides studied. Evidently, the method for the insertion of methylene groups into dialkyl sulphides can be used successfully for the qualitative identification and for the analysis of alkanes. The observed deviation of the relative concentrations of isomeric sulphides in the "methylenates" from the theoretically predicted values demonstrates that in all instances the degree of methylene insertion differs from the theoretical value by less than one order of magnitude. The quantitative analysis of the composition of the "methylenates" obtained results in a mean-square error varying from ± 2.0 to ± 2.5 .

We have used the structural group analysis of the results of methylene insertion reactions on 17 dialkyl sulphides (with the exception of dimethyl sulphide) in order to evaluate the degree of methylene insertion at the C-H bonds of various types in thiaalkanes. The composition of a sulphide produced by a methylene insertion reaction is determined by the number of C-H bonds in the starting sulphide. Each

TABLE II
 PRODUCTS OF METHYLENE INSERTION REACTIONS ON SOME DIALKYL SULPHIDES

Starting dialkyl sulphide	Product	Log t_{R_x}	Concentration (wt.%) (relative)		
			Theoretical	Experimental	Difference
C-S-C-C-C (C ₄ H ₁₀ S)	C-S-C-C-C-C	1.4771	30.0	38.0	+ 8.0
	C-C-S-C-C-C	1.4314	30.0	29.0	- 1.0
	C-S-C-C-C	1.4099	20.0	13.0	- 7.0
	$\begin{array}{c} \\ C \\ \\ C-S-C-C-C \end{array}$	1.3892	20.0	20.0	0
C-C-S-C-C (C ₅ H ₁₂ S)	C-C-S-C-C-C	1.6107	50.0	59.0	+ 9.0
	$\begin{array}{c} \\ C \\ \\ C-C-S-C-C-C \end{array}$	1.5775	25.0	25.0	0
	$\begin{array}{c} \\ C \\ \\ C-C-S-C-C \end{array}$	1.4472	8.3	4.0	- 4.3
	$\begin{array}{c} \\ C \\ \\ C-C-S-C-C \\ \quad \\ C \quad C \end{array}$	1.4281	16.7	12.0	- 4.7
C-C-S-C-C-C (C ₆ H ₁₄ S)	C-C-S-C-C-C-C	1.8129	43.5	52.0	+ 8.5
	$\begin{array}{c} \\ C \\ \\ C-C-C-S-C-C-C \end{array}$	1.7672	21.3	21.0	- 0.3
	$\begin{array}{c} \\ C \\ \\ C-C-S-C-C-C \end{array}$	1.7364	7.0	5.0	- 2.0
	$\begin{array}{c} \\ C \\ \\ C-C-S-C-C-C \\ \\ C \end{array}$	1.7033	14.1	11.0	- 3.1
	$\begin{array}{c} \quad \\ C \quad C \\ \quad \\ C-C-S-C-C-C \\ \quad \\ C \quad C \end{array}$	1.6484	14.1	11.0	- 3.1

of the isomers produced has only one type of the C-H bond. The composition may be written as follows:



where a , b , c , A , B and C are the numbers of the respective groups. This composition corresponds to the following number of the C-H bonds of various types:

$$3a + 2b + 1c + 3A + 2B + 1C = \Sigma C-H$$

We assume that in the methyl groups distant from the sulphur atom, the reactivity of the C-H bonds corresponds strictly to their number. Taking this value as a reference, we could evaluate the relative degree of methylene insertion at the C-H bonds of the other types from the chromatograms for the "methylenates". Table III presents the results of such a treatment for 17 "methylenates" of dialkyl sulphides.

TABLE III

RELATIVE DEGREE OF METHYLENE INSERTION AT THE C-H BONDS FOR VARIOUS DIALKYL SULPHIDES

The figures given indicate the number of C-H bonds/degree of methylene insertion.

Isomer	<i>CH</i> ₃	<i>CH</i> ₂	<i>CH</i>	<i>CH</i> ₃ <i>S</i>	<i>CH</i> ₂ <i>S</i>	<i>CHS</i>	Total	
	No. of C-H bonds in group							
	3	2	1	3	2	1		
C-S-C-C	3/3	—	—	3/2.8	2/1.7	—	8/7.5	
C-S-C-C	6/6	—	—	3/2.0	—	1/0.7	10/8.7	
C								
C-C-S-C-C	6/6	—	—	—	4/2.4	—	10/8.4	
C-S-C-C-C	3/3	2/1.7	—	3/2.3	2/1.0	—	10/8.0	
C								
C-S-C-C	9/9	—	—	3/2.5	—	—	12/11.5	
C								
C-C-S-C-C	9/9	—	—	—	2/1.3	1/0.8	12/11.1	
C								
C-S-C-C-C	6/6	2/1.9	—	3/2.2	—	1/0.8	12/10.9	
C								
C-S-C-C-C	6/6	—	1/0.9	3/2.4	2/1.4	—	12/10.7	
C								
C-C-S-C-C-C	6/6	2/1.5	—	—	4/2.1	—	12/9.6	
C-S-C-C-C-C	3/3	4/2.8	—	3/2.2	2/1.1	—	12/9.1	
C-C-S-C-C	12/12	—	—	—	—	2/1.6	14/13.6	
C								
C-C-S-C-C-C	9/9	2/1.9	—	—	2/1.7	1/0.6	14/13.2	
C								
C-C-S-C-C-C	9/9	2/1.4	—	—	2/1.4	1/0.6	14/12.4	
C								
C-C-S-C-C-C	9/9	—	1/0.7	—	4/2.7	—	14/12.4	
C								
C-C-C-S-C-C-C	6/6	4/3.0	—	—	4/2.2	—	14/11.2	
C-C-S-C-C-C-C	6/6	4/3.4	—	—	4/2.2	—	14/11.6	
C-S-C-C-C-C-C	3/3	6/4.4	—	3/2.4	2/1.1	—	14/10.9	

Referring the results obtained to one C-H bond and averaging them over the different types, we arrived at the following conclusion: the degree of methylene insertion at one C-H bond in the methyl group distant from the sulphur atom is 1 (standard), in the CH₂S and CHS groups it is 0.7 ± 0.1 and in the CH₂ and CH groups it is 0.8 ± 0.1 . The methylene insertion reactions of dialkyl sulphides with diazomethane revealed a noticeable inhibitory effect of the sulphur atom; for the secondary and tertiary alkyl groups it is about 15% (relative), and for the methyl group 12%. Unexpectedly, 12% inhibition was observed for the methylene insertion reactions of the CH₂ and CH groups 1-3 carbon atoms distant from the sulphur atom.

CONCLUSION

Methylene insertion reactions on 18 dialkyl sulphides with diazomethane has been carried out for the first time. Gas-liquid chromatography has been used to demonstrate the presence in the products of all the theoretically predicted dialkyl sulphides with numbers of carbon atoms exceeding by one the corresponding numbers in the starting sulphides. The products of the methylene insertion reactions have been used to determine the logarithms of the retention times and retention indices on tricresyl phosphate at 100° for 47 dialkyl sulphides. Methylene insertion reactions are recommended for use in the qualitative analysis of thiaalkanes and their mixtures. A rough quantitative description has been given of the effect of the sulphur atom in dialkyl sulphides on the relative reactivity of the C-H bonds in the methylene insertion reaction.

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