

CHROM. 9108

## APPLICATION OF METHYLENE-INSERTION REACTIONS TO CYCLIC SULPHIDES ( $C_4H_8S$ , $C_5H_{10}S$ AND $C_6H_{12}S$ ) TO PRODUCE STANDARD COMPOUNDS FOR GAS CHROMATOGRAPHY

G. D. GAL'PERN, N. I. GOLLANDSKIKH and G. N. GORDADZE

*A. V. Topchiev Institute of Petrochemical Synthesis, U.S.S.R. Academy of Sciences, Moscow (U.S.S.R.)*

(Received January 27th, 1976)

---

### SUMMARY

The methylenation of thiacyclanes in order to obtain standard substances for analysing isomeric thiacyclanes and their mixtures by gas-liquid chromatography on capillary columns is described. Retention indices are reported for 29 thiacyclopentanes and 22 thiacyclohexanes at 85° and 100° on tricresyl phosphate and at 100° on OV-101.

---

### INTRODUCTION

The reaction of methylene insertion of saturated hydrocarbons, first described by Doering and Buttery<sup>1</sup>, involves homolytic addition of methylene-groups formed during photolysis of diazomethane along the C-H bonds. The insertion of such groups along all the C-H bonds of the irradiated sample produces a mixture of the corresponding homologues and their isomers. The successful application of the methylenation reaction in solving problems associated with the stereochemistry of cyclic hydrocarbons has been described<sup>2</sup>. We have shown<sup>3</sup> that it is possible to methylenate dialkyl sulphides, and some facts governing this reaction were noted. Thiacyclopentane (TCP) and thiacyclohexane (TCH) have also been methylenated<sup>4</sup>.

The purpose of this work was to ascertain whether methylenation of cyclic sulphides could be used to prepare thiacyclane mixtures for use as standards in gas-liquid chromatography (GLC), and an attempt has been made to study factors affecting the methylenation of thiacyclanes.

TCP and its 2- and 3-methyl-derivatives, TCH and its 2-, 3- and 4-methyl-derivatives, the *cis*- and *trans*-isomers of 2,5-dimethyl-TCP and 2-ethyl-TCP were used for methylenation.

### EXPERIMENTAL

#### *Production of thiacyclanes*

The compounds synthesized in our laboratory were: TCP and TCH, 2-methyl-TCP and *cis*- and *trans*-2,5-dimethyl-TCP (obtained by following the procedure of

Whitehead *et al.*<sup>5</sup>); 3-methyl-TCH in combination with 2,2-dimethyl-TCP (obtained by following the procedure of Kondo and Negishi<sup>6</sup>); 3-methyl-TCP, 4-methyl-TCH, and 2-methyl-TCH with 2-ethyl-TCP (obtained by following the procedure of Volynskii *et al.*<sup>7</sup>). The products were mixtures of isomers and required further purification.

#### *Purification of thiacyclanes*

Preparative GLC on a PAKhV-05 chromatograph (designed at the Special Design Bureau, Institute of Petrochemical Synthesis, USSR Academy of Sciences was used for purification. The column (total length 9 m) was of stainless steel (2 m × 25 mm; 2 m × 8 mm; 1 m × 4 mm), and was packed with 15% of polyethylene glycol adipate on INZ-600 diatomite brick (size fraction 0.30–0.65 mm), the support having been calcined at 1050° for 3 h. The volume of sample introduced ranged from 0.6 to 1 ml, and the carrier gas (helium) flow-rate was 120–180 ml/min. The column was operated at 100 to 150°. After purification, the following products were obtained: TCH and TCP (99% pure); 2-methyl-TCP (97% pure, with 3-methyl-TCP as impurity); 3-methyl-TCP (98% pure, with 2-methyl-TCP as impurity); *cis*-2,5-dimethyl-TCP (95% pure, with the *trans*-isomer as impurity) and *trans*-2,5-dimethyl-TCP (96% pure, with the *cis*-isomer as impurity); 2-ethyl-TCP (98% pure, with 2-methyl-TCH as impurity); 2-methyl-TCH (98% pure, with 2-ethyl-TCP as impurity); 3-methyl-TCH (98% pure, with 2,2-dimethyl-TCP as impurity); and 4-methyl-TCH (97% pure, with 2-methyl-TCH as impurity).

#### *Methylenation of thiacyclanes*

Methylenation was carried out in a quartz test tube (2 ml in volume) equipped with a continuous cooling-water jacket. The source of external irradiation was a mercury-quartz lamp, type PRK-2, as described previously<sup>3</sup>; the applied potential (215 V) was maintained constant throughout the reaction. The distance from the source to the reactor was also kept constant. Methylenation of thiacyclanes proceeded more slowly than that of dialkyl sulphides: 3 h was needed for the reaction mixture to decolorize in a single experiment, which is approximately twice the time needed with thia-alkanes. In all instances thiacyclanes were methylenated twice, as described previously<sup>3</sup>.

#### *Analysis of methylenation products*

This was accomplished with use of a Tsvet-101 chromatograph with 50 and 100-m high-efficiency capillary columns (0.25 mm I.D.) coated with either tricresyl phosphate (operated at 85° and 100°) or OV-101 (operated at 100°). The carrier gas was hydrogen (flow-rate 1.6 ml/min when using tricresyl phosphate, and 1.2 ml/min with OV-101), and detection was by flame ionization. The volume of sample introduced was 8  $\mu$ l.

#### *Identification of methylenation products*

Thiacyclanes were identified by mixing the individual compounds to give "methylenates", of known composition; reaction chromatography and GLC-mass spectrometry (MS) were also regularly used. Thus, when identifying the "methylenate" of 2-methyl-TCP, such standard compounds as 2,3-dimethyl-TCP, the sepa-

rate *cis*- and *trans*-isomers, *cis*- and *trans*-2,5-dimethyl-TCP, 2,2-dimethyl-TCP and 2-ethyl-TCP were used. Stereoisomers of 2,5-dimethyl-TCP were assigned to the *cis*- or *trans*-series according to the principles of Whitehead *et al.*<sup>5</sup> (by means of which it was established that *meso*-dibromides produce *cis*-2,5-dimethyl-TCP) and also on the basis of the configurational isomerization of both stereoisomers carried out by us. The use of <sup>1</sup>H nuclear magnetic resonance (NMR) and <sup>13</sup>C NMR did not permit unambiguous identification of the types of these isomers. Assignment of the stereoisomers of 2,3-dimethyl-TCP to the *cis*- or *trans*-series was based on configurational isomerization (this will be described in detail in a separate paper). Mixing the "methylenates" of 2- and 3-methyl-TCP made it possible to identify 2,3- and 2,4-dimethyl-TCP. 2,4-Dimethyl-TCP stereoisomers were assigned to the *cis*- or *trans*-series as before<sup>3</sup>, *i.e.*, the lower-boiling isomer was assumed to have the *cis*-configuration. As an example, Fig. 1 shows a typical chromatogram of the separation of 2-, 3- and 4-methyl-TCH methylenation products on tricresyl phosphate at 85°. Methylenation of both 2- and 3-methyl-TCH yields *cis*- and *trans*-2,3- and 2,5-dimethyl-TCH. These compounds were identified from the b.p. calculated from the retention indices on OV-101 and from the data of Beiko and Gusinskaya<sup>8</sup>. By mixing pairs of the methylenation

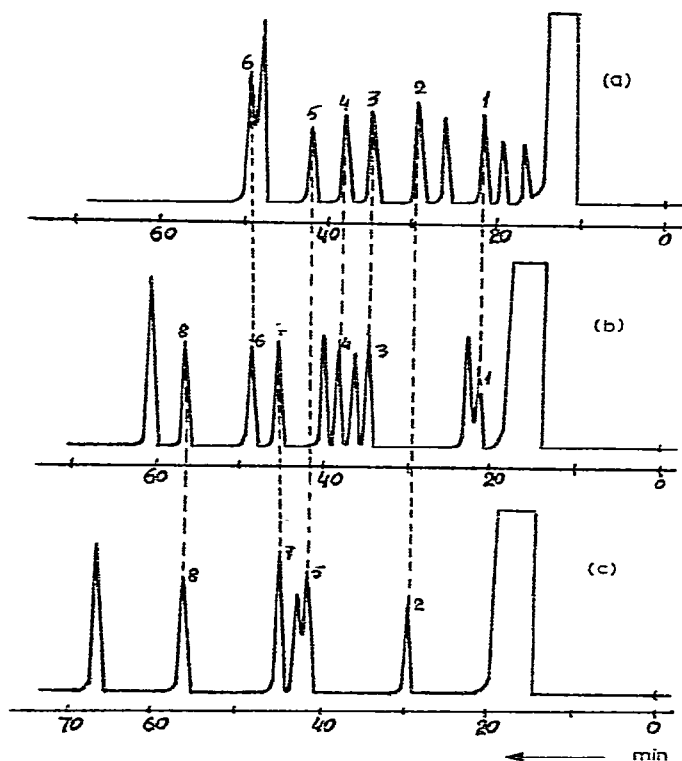


Fig. 1. Chromatograms (tricresyl phosphate column at 85°) of methylenation products from (a) 2-methyl-TCH, (b) 3-methyl-TCH and (c) 4-methyl-TCH. 1 = 2,5-Dimethyl-TCH (*trans*); 2 = 2,4-dimethyl-TCH (*cis*); 3 = 2,5-dimethyl-TCH (*cis*); 4 = 2,3-dimethyl-TCH (*trans*); 5 = 2,4-dimethyl-TCH (*trans*); 6 = 2,3-dimethyl-TCH (*cis*); 7 = 3,4-dimethyl-TCH (*trans*); 8 = 3,4-dimethyl-TCH (*cis*).

products of 2-methyl-TCH, 3-methyl-TCH and 4-methyl-TCH; it was possible to identify 2,4- and 3,4-dimethyl-TCH; they were assigned to *cis*- or *trans*-series by analogy with the assignment of alkylcyclohexanes and by comparison with the data of Beiko and Gusinskaya<sup>8</sup>. Having exactly determined the configurational *cis*- and *trans*-isomers of 2,5-dimethyl-TCP, we could identify the ethylmethyl-TCP and trimethyl-TCP series in the methylenation products.

In several instances, chromatographic hydrodesulphurization was applied to characterize the products of methylenation. This process was conducted in a micro-reactor incorporated into the gas line of the Tsvet-101 chromatograph (see ref. 3); 10% of platinum applied to INZ-600 diatomite (0.315-mm fraction) served as the catalyst, and the temperature in the micro-reactor was 275°. The methylenation products were analysed at 82° on a stainless-steel column with OV-101 as stationary phase and a hydrogen pressure of 1.2 atm. The volume of sample introduced into the micro-reactor was 0.3  $\mu$ l. The hydrocarbons formed were identified, with the help of *n*-hexane isomerisate, by using the data of Bryanskaya *et al.*<sup>9</sup>.

To obtain additional characteristics of the methylenation products, we used GLC-MS with an LKB-2091 apparatus and an ionization energy of 70 eV. The conditions of introducing the sample into the column were similar to those used in GLC, but helium was used as carrier gas instead of hydrogen. From the mass spectra, we were able readily to identify monoalkyl-substituted thiacyclanes and to ascertain the number of substituents in di- and tri-alkylthiacyclanes.

An essential condition for identification is the complete separation of *cis*- and *trans*-isomers. This was achieved by using high-efficiency capillary columns and two stationary phases and by carrying out the separation at different temperatures.

## RESULTS

The composition of the methylenation products of thiacyclopentanes is shown in Table I; that of thiacyclohexanes is shown in Table II. Theoretical values for the relative concentrations of the components were obtained by assuming an equal degree of initial thiacyclane transformation along all the C-H bonds. The values in Tables I and II are averages from four to ten experiments for each of the "methylenates" and from the results of ten measurements on every chromatogram. The fact that the mean square error is relatively large makes it impossible to estimate the selectivity of thiacyclane methylenation. In the first approximation for the methylenation of any of the thiacyclanes listed, it can be disregarded. The apparent differences between the methylenation of thiacyclanes and that of thia-alkanes are due to the greater number of isomers in the "methylenates" and, therefore, a higher relative error of measurements. A substantially better sensitivity and greater accuracy are required in order to detect possible slight differences in the rates of methylenation along C-H bonds that differ in position relative to the sulphur atom.

For all the thiacyclanes studied we have calculated the retention indices (reproducibility  $\pm 1$ ), the differences between these indices for the polar phase at two temperatures [ $\Delta I_i^{t_{cp}}$  see ref. 10)], the differences between these indices for the polar and non-polar phase at 100°, values of  $\Delta I_i$  and b.p.; the results are shown in Table III. It can be seen from this Table that *cis*-3,4-dimethyl-TCP is not separated from 4-methyl-TCH on tricresyl phosphate at 85°, but that these compounds are better

TABLE I  
COMPOSITION OF METHYLENATION PRODUCTS OF THIACYCLOPENTANES

Methylenation product	Log $t'_{Rz}$ *	Concentration (wt.%)		Mean square error (%)
		Theoretical	Experimental	
<i>From thiacyclopentane (TCP)</i>				
2-Methyl-TCP	1.3010	50	48	0.9
3-Methyl-TCP	1.4150	50	52	0.9
<i>From 2-methyl-TCP</i>				
2-Ethyl-TCP	1.5911	30	33	0.6
2,2-Dimethyl-TCP	1.3617	10	9	0.8
2,3-Dimethyl-TCP ( <i>cis</i> )	1.5740	10	9	0.8
2,3-Dimethyl-TCP ( <i>trans</i> )	1.4440	10	10	0.5
2,4-Dimethyl-TCP ( <i>cis</i> )	1.4314	10	9	0.8
2,4-Dimethyl-TCP ( <i>trans</i> )	1.4698	10	9	0.5
2,5-Dimethyl-TCP ( <i>cis</i> )	1.3892	10	10	0.5
2,5-Dimethyl-TCP ( <i>trans</i> )	1.3766	10	11	0.8
<i>From 3-methyl-TCP</i>				
3-Ethyl-TCP	1.7076	30	34	0.6
3,3-Dimethyl-TCP	1.5315	10	10	0.5
2,3-Dimethyl-TCP ( <i>cis</i> )	1.5740	10	9	0.8
2,3-Dimethyl-TCP ( <i>trans</i> )	1.4440	10	10	0.5
2,4-Dimethyl-TCP ( <i>cis</i> )	1.4314	10	9	0.6
2,4-Dimethyl-TCP ( <i>trans</i> )	1.4698	10	10	0.5
3,4-Dimethyl-TCP ( <i>cis</i> )	1.6335	10	8	0.6
3,4-Dimethyl-TCP ( <i>trans</i> )	1.6021	10	10	0.6
<i>From 2,5-dimethyl-TCP (cis)</i>				
5-Ethyl-2-methyl-TCP ( <i>cis</i> )	1.5798	50	51	0.9
2,2,5-Trimethyl-TCP	1.4843	16.6	16	0.8
2,3,5-Trimethyl-TCP ( <i>cis,cis</i> )	1.6128	16.7	16	1.0
3,3,5-Trimethyl-TCP ( <i>trans,cis</i> )	1.5011	16.7	17	1.0
<i>From 2,5-Dimethyl-TCP (trans)</i>				
5-Ethyl-2-methyl-TCP ( <i>trans</i> )	1.6304	50	54	1.0
2,2,5-Trimethyl-TCP	1.4843	16.6	15	0.9
2,3,5-Trimethyl-TCP ( <i>cis,trans</i> )	1.5563	16.7	16	0.8
2,3,5-Trimethyl-TCP ( <i>trans,trans</i> )	1.5159	16.7	15	0.9
<i>From 2-ethyl-TCP</i>				
2-Propyl-TCP	1.8998	25	26	0
2-Isopropyl-TCP	1.7482	16.9	17	0.7
2-Ethyl-2-methyl-TCP	1.7067	8.3	7	0.4
2-Ethyl-3-methyl-TCP ( <i>trans</i> )	1.6972	8.3	7	0.5
2-Ethyl-3-methyl-TCP ( <i>cis</i> )	1.7709	8.3	7	0.8
2-Ethyl-4-methyl-TCP ( <i>trans</i> )	1.7160	8.3	9	0.5
2-Ethyl-4-methyl-TCP ( <i>cis</i> )	1.6580	8.3	9	0.7
2-Ethyl-5-methyl-TCP ( <i>trans</i> )	1.5798	8.3	9	0.7
2-Ethyl-5-methyl-TCP ( <i>cis</i> )	1.6304	8.3	9	0.6

\* Log  $t'_{Rz}$ :  $t'_R$  is  $t_R - t_0$ ;  $t_0$  is the retention time for methane and  $t_R$  is the retention time of thiacycane on the column with tricresyl phosphate at 100°.

TABLE II  
COMPOSITION OF METHYLENATION PRODUCTS OF THIACYCLOHEXANES

Methylenation product	Log $t'_{Rz}$	Concentration (wt.%) (relative)		Mean square error (%)
		Theoretical	Experimental	
<i>From thiacyclohexane (TCH)</i>				
2-Methyl-TCH	1.5051	40	39	2.0
3-Methyl-TCH	1.5798	40	40	1.7
4-Methyl-TCH	1.5966	20	21	2.0
<i>From 2-methyl-TCH</i>				
2-Ethyl-TCH	1.8929	25	25	1.0
2,2-Dimethyl-TCH	1.6128	8.3	7	0.9
2,3-Dimethyl-TCH ( <i>trans</i> )	1.7364	8.3	9	0.9
2,3-Dimethyl-TCH ( <i>cis</i> )	1.8261	8.3	8	0.8
2,4-Dimethyl-TCH ( <i>trans</i> )	1.7604	8.4	8	1.0
2,4-Dimethyl-TCH ( <i>cis</i> )	1.6902	8.4	8.5	0.5
2,5-Dimethyl-TCH ( <i>trans</i> )	1.6628	8.3	9	0.7
2,5-Dimethyl-TCH ( <i>cis</i> )	1.7324	8.3	8.5	0.3
2,6-Dimethyl-TCH ( <i>trans</i> )	1.6812	8.3	9	0.9
2,6-Dimethyl-TCH ( <i>cis</i> )	1.6232	8.3	8	0.9
<i>From 3-methyl-TCH</i>				
3-Ethyl-TCH	1.9138	25	25	0.7
3,3-Dimethyl-TCH	1.7076	8.4	9	0.5
2,3-Dimethyl-TCH ( <i>trans</i> )	1.7364	8.3	8	0.9
2,3-Dimethyl-TCH ( <i>cis</i> )	1.8261	8.3	8	0.9
3,4-Dimethyl-TCH ( <i>trans</i> )	1.7924	8.4	9	0.7
3,4-Dimethyl-TCH ( <i>cis</i> )	1.8976	8.4	9	0.7
2,5-Dimethyl-TCH ( <i>trans</i> )	1.6628	8.3	7	0.6
2,5-Dimethyl-TCH ( <i>cis</i> )	1.7324	8.3	8	0.9
3,5-Dimethyl-TCH ( <i>trans</i> )	1.7634	8.3	8	0.6
3,5-Dimethyl-TCH ( <i>cis</i> )	1.7160	8.3	9	0.6
<i>From 4-methyl-TCH</i>				
4-Ethyl-TCH	1.9420	25.0	25	0
4,4-Dimethyl-TCH	1.7709	8.3	8	1.5
2,4-Dimethyl-TCH ( <i>trans</i> )	1.7604	16.7	16	1.0
2,4-dimethyl-TCH ( <i>cis</i> )	1.6902	16.6	17	1.5
3,4-dimethyl-TCH ( <i>trans</i> )	1.7924	16.7	17	0.8
3,4-dimethyl-TCH ( <i>cis</i> )	1.8976	16.7	17	0.5

separated at 100°, and readily separated on the non-polar OV-101. The use of two temperatures and different phases gives good identification of thiacyclanes whose retention indices differ by 1. For example, these indices for *trans*-2-ethyl-3-methyl-TCP and 3-ethyl-TCH differ by 1 on tricresyl phosphate at 85° and by 4 at 100°. On OV-101, this difference reaches as much as 16, but the sequence of elution changes: first 3-ethyl-TCH and then *trans*-2-ethyl-3-methyl-TCP. Thus, the use of two temperatures and two columns with stationary phases of different polarities makes it possible to identify the components of such complex mixtures as the "methyleneates" of thiacyclanes. This is especially important when identifying the components of sulphurous concentrates obtained from gasoline fractions.

TABLE III

## RETENTION INDICES AND BOILING-POINTS OF THIACYCLANES

$I_{85}^{TCP}$ ,  $I_{100}^{TCP}$  and  $I_{100}^{OV-101}$  are the retention indices on a tricresyl phosphate column at 85 and 100° and an OV-101 column at 100°, respectively. The b.p. values were determined graphically from the results on the OV-101 column at 100°:  $\Delta I_t = I_{100}^{TCP} - I_{85}^{TCP}$ ;  $\Delta I_L = I_{100}^{TCP} - I_{100}^{OV-101}$ .

Thiacyclane	$I_{85}^{TCP}$	$I_{100}^{TCP}$	$\Delta I_t$	$I_{100}^{OV-101}$	$\Delta I_L$	B.p. (°C)
Thiacyclopentane (TCP)	992	1019	27	805	214	122
2-Methyl-TCP	1013	1044	31	851	193	133
2,2-Dimethyl-TCP	1036	1065	29	887	188	139
2,5-Dimethyl-TCP ( <i>trans</i> )	1040	1070	30	881	189	141
2,5-Dimethyl-TCP ( <i>cis</i> )	1044	1074	30	885	189	142
3-Methyl-TCP	1048	1083	35	869	214	138
2,4-Dimethyl-TCP ( <i>cis</i> )	1070	1089	19	895	194	145
Thiacyclohexane (TCH)	1073	1083	13	880	203	141
2,3-Dimethyl-TCP ( <i>trans</i> )	1076	1094	18	899	195	146
2,4-Dimethyl-TCP ( <i>trans</i> )	1080	1102	22	904	198	147
3,3-Dimethyl-TCP	1083	1123	40	902	221	146
2,3-Dimethyl-TCP ( <i>cis</i> )	1087	1128	41	980	220	150
2,2,5-Trimethyl-TCP	1097	1107	10	905	202	147
2,3,5-Trimethyl-TCP ( <i>trans,cis</i> )	1101	1113	12	941	172	156
2,3,5-Trimethyl-TCP ( <i>trans,trans</i> )	1110	1118	8	947	171	158
2-Methyl-TCH	1115	1120	5	924	196	152
3,4-Dimethyl-TCP ( <i>trans</i> )	1119	1148	29	932	216	155
2,3,5-Trimethyl-TCP ( <i>cis,trans</i> )	1129	1134	5	964	170	162
2-Ethyl-TCP	1130	1144	14	945	199	157
5-Ethyl-2-methyl-TCP ( <i>cis</i> )	1133	1146	13	967	179	163
2,2-Dimethyl-TCH	1134	1151	17	941	210	157
3-Methyl-TCH	1137	1140	3	939	201	156
2,3,5-Trimethyl-TCP ( <i>cis,cis</i> )	1139	1151	12	975	176	165
3,4-Dimethyl-TCP ( <i>cis</i> )	1142	1158	16	950	208	159
4-Methyl-TCH	1142	1146	4	940	206	156
2,6-Dimethyl-TCH ( <i>cis</i> )	1145	1155	10	957	198	160
5-Ethyl-2-methyl-TCP ( <i>trans</i> )	1147	1159	12	977	182	166
2-Ethyl-4-methyl-TCP ( <i>cis</i> )	1149	1167	18	979	188	166
2-Ethyl-3-methyl-TCP ( <i>trans</i> )	1152	1180	28	986	194	168
3-Ethyl-TCP	1153	1184	31	970	214	164
2,5-Dimethyl-TCH ( <i>trans</i> )	1154	1168	14	973	195	164
2-Ethyl-2-methyl-TCP	1155	1183	28	994	189	169
3,3-Dimethyl-TCH	1157	1184	27	989	195	169
2,6-Dimethyl-TCH ( <i>trans</i> )	1161	1175	14	978	197	166
2-Ethyl-4-methyl-TCP ( <i>trans</i> )	1166	1186	20	997	189	171
2,4-Dimethyl-TCH ( <i>cis</i> )	1168	1178	10	998	190	168
3,5-Dimethyl-TCH ( <i>cis</i> )	1171	1186	15	989	197	169
2-Isopropyl-TCP	1174	1197	23	1014	183	174
2,5-Dimethyl-TCH ( <i>cis</i> )	1180	1192	12	997	195	171
2,3-Dimethyl-TCH ( <i>trans</i> )	1184	1193	9	998	195	171
2,4-Dimethyl-TCH ( <i>trans</i> )	1189	1202	13	1008	194	174
3,5-Dimethyl-TCH ( <i>trans</i> )	1191	1203	12	1004	199	173
2-Ethyl-3-methyl-TCP ( <i>cis</i> )	1192	1205	13	999	206	171
4,4-Dimethyl-TCH	1193	1205	8	1008	197	174
3,4-Dimethyl-TCH ( <i>trans</i> )	1206	1213	7	1015	198	175
2-Propyl-TCP	1208	1252	44	1037	215	181
2-Ethyl-TCH	1210	1221	11	1024	197	177
2,3-Dimethyl-TCH ( <i>cis</i> )	1211	1225	14	1022	203	177
3,4-Dimethyl-TCH ( <i>cis</i> )	1231	1251	20	1039	212	181
3-Ethyl-TCH	1238	1257	19	1047	210	184
4-Ethyl-TCH	1247	1267	20	1050	217	185

By using literature values for the b.p.<sup>5</sup> of TCP, 2-methyl-TCP, 2-ethyl-TCP and 3-propyl-TCP, we were able to establish that there was a linear relationship between the retention indices and the b.p., for the non-polar OV-101 at 100° (see Fig. 2); the correlation coefficient for the straight line is 0.99. From this graph, approximate b.p. values have been found for all the thiacyclanes studied; these are shown in Table III.

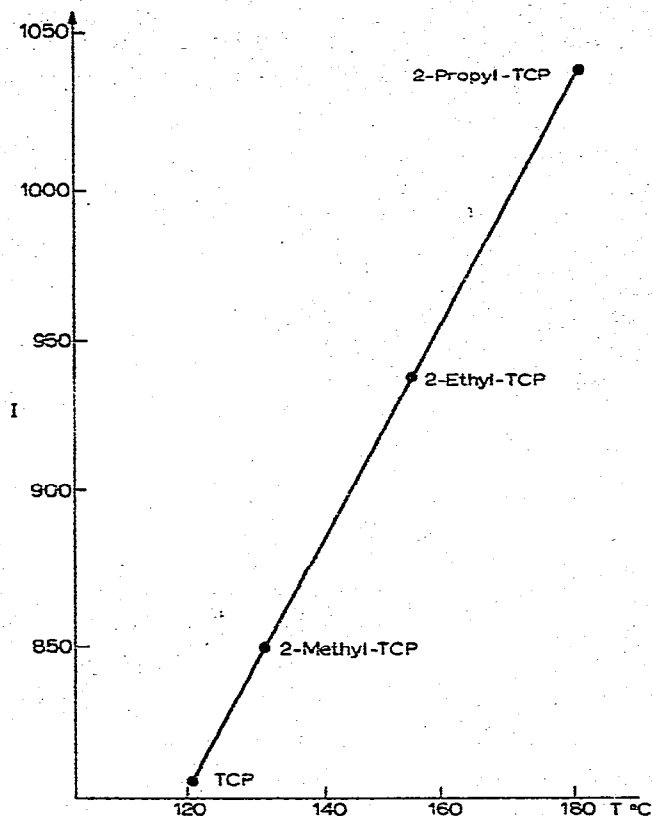


Fig. 2. Dependence of retention indices of thiacyclanes on their b.p. (OV-101, 100°).

## CONCLUSIONS

Methylenation of six thiacyclopentanes and four thiacyclohexanes with diazomethane has been carried out for the first time. The presence in the methylenation products of all the theoretically possible thiacyclanes with one more carbon atom than in the original thiacyclane has been established by GLC. With the help of methylenation products, approximate b.p. and retention indices on tricresyl phosphate have been determined at 85° and 100° (and on OV-101 at 100°) for 29 thiacyclopentanes of composition ranging from  $C_4H_8S$  to  $C_7H_{14}S$  and 22 thiacyclohexanes ranging in composition from  $C_5H_{10}S$  to  $C_7H_{14}S$ . Methylenation of thiacyclanes is recommended



for obtaining the qualitative analytical characteristics of thiacyclanes and their mixtures. The products of thiacyclane methylenation can be used as standard substances in the qualitative analysis of complex thiacyclane mixtures.

#### ACKNOWLEDGEMENTS

We would like to express our profound gratitude to Dr. N. P. Volynskii and L. P. Shcherbakova for the thiacyclanes specially synthesized for our experiments, and to Dr. Ye. N. Karaulova, T. A. Bardina and O. S. Minayeva for providing thiacyclane samples. The GLC-MS was performed by Zaikin, Candidate of Chemical Sciences, who deserves special appreciation.

#### REFERENCES

- 1 W. E. Doering, R. G. Buttery, R. G. Laughlin and N. Chandhuri, *J. Amer. Chem. Soc.*, 78 (1956) 3224.
- 2 I. M. Makarova, V. A. Zakharenko, S. S. Berman, O. A. Aref'ev and A. A. Petrov, *Neftekhimiya*, 6 (1966) 513.
- 3 G. D. Gal'pern, N. I. Gollandskikh and G. N. Gordadze, *J. Chromatogr.*, 109 (1975) 119.
- 4 G. N. Gordadze, *Zh. Obshch. Org. Khim.*, 7 (1971) 1999.
- 5 E. V. Whitehead, R. H. Dean and F. A. Fidler, *J. Amer. Chem. Soc.*, 73 (1951) 3632.
- 6 K. Kondo and A. Negishi, *Abstr. Third Int. Congr. Heterocyclic Chem., Sendai, Japan, 1971*, p. 589.
- 7 N. P. Volynskii, G. D. Gal'pern and V. V. Smolyaninov, *Neftekhimiya*, 3 (1963) 482.
- 8 O. A. Beiko and S. L. Gusinskaya, *Neftekhimiya*, 11 (1971) 775.
- 9 E. K. Bryanskaya, Z. K. Olenina and A. A. Petrov, in Coll. Art. 2, "Methods of Analysing Organic Petroleum Compounds, Their Mixtures and Derivatives", Nauka, Moscow, 1969, p. 7.
- 10 G. Schomburg and G. Diefman, *Anal. Chem.*, 45 (1973) 647.