

APPLICATION OF OXYMERCURATION-DEMERCURATION FOR ANALYSIS OF OLEFINS IN PYROLYSIS GASOLINE*

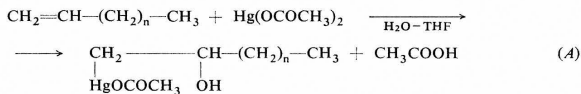
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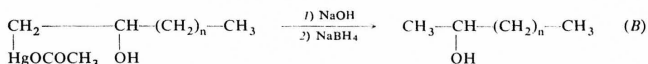
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Substituted ethylenes were converted to secondary and tertiary alcohols by employing the oxymercuration-demercuration method (OM-DM). The reactivity of mercury(II) acetate with ethylenes in aqueous-tetrahydrofuran solutions is similar to that in methanolic solutions, the presence of paraffinic and aromatic hydrocarbons does not interfere. The OM-DM reaction is selective for asymmetrically mono-, di-, and trisubstituted ethylenes. The method was used for analysis of fractions of pyrolysis gasoline, b.p. 23–43°C. The alcohols isolated were identified by means of mass spectrometry.

The subject of our study is the analysis of ethylenic hydrocarbons present in products of pyrolysis of brown coal and petroleum¹⁻³ in mixtures with paraffinic and aromatic hydrocarbons and substances of nonhydrocarbon nature. Ethylenic hydrocarbons have been determined in similar products together with other substances present by means of gas chromatography or other physical techniques⁴⁻⁷. For a quantitative determination of olefins in products of thermal cracking of Kuwaitian petroleum, their conversion to alcohols was applied by hydroboration and oxidation with hydrogen peroxide in an alkaline medium^{8,9}. In our previous works¹⁻³, for the separation of higher-boiling olefins C₁₀–C₁₆ we made use of the high polarity of their methoxymercurates; in this form we separated them as a group from the low-polar paraffinic and aromatic hydrocarbons on an Al₂O₃ column, regenerated the olefins and analyzed them by ozonization. In the present work we converted the olefins to alcohols by applying the oxymercuration-demercuration (OM-DM) method¹⁰⁻¹⁴ according to the scheme



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The conversion of low-boiling olefins present in the fractions of b.p. 20–60°C to alcohols is very convenient, because it constitutes a way of circumventing the problem of injection of the highly volatile (partly gaseous) hydrocarbons.

The aim of this work was to find out, which types of ethylenes are amenable to the to the OM-DM conversion to the alcohols, how many side products are formed during that reaction, and how the alcohols formed separate from the paraffinic and aromatic hydrocarbons. In addition, we wanted to examine the practical applicability of the above hydroxylation in the presence of paraffinic and aromatic hydrocarbons and to test the OM-DM technique with a fraction of pyrolysis gasoline. The analyses of other fractions are to be published later. As in our previous work¹⁵ we compared,

TABLE I

Characterization of the Columns Employed

Stainless steel columns, i.d. 0.3 cm, were used.

Column		Carrier grain size, mm	Stationary phase introduced, % m/m
designation	length, cm		
A ^a	250	Chromaton-N-AW-DMCS (0.16–0.20)	Apiezon L (4)
B	120	Chromaton-N-AW-DMCS (0.20–0.25)	Carbowax 6000 (15)
C	80 ^b	Chezasorb-II (0.10–0.20)	Carbowax 20 M (15)
D	250	Chromaton-N-AW (0.125–0.160)	Diethylene glycolsuccinate (15)
E	360	Chezasorb-II (0.20–0.30)	β,β-oxypionitrile (20)
F	360	Chromaton-N-AW-DMCS (0.125–0.160)	Carbowax 600 (15)
G	360	Chromaton-N-AW-DMCS (0.20–0.25)	Carbowax 6000 (15)
H ^a	250	Chromaton-W (0.129–0.71)	Carbowax 20 M (10)

^a Glass column; ^b i.d. 0.6 cm.

TABLE II

Results of Analyses of 6-Tridecene (first row) and 7-Tridecanol (second row) on the Columns A and B^a

Introduced %	Found, %		Difference, %	
	A	B	A	B
93.3	97.1	100	+3.8	+6.7
6.7	2.9	0	-3.8	-6.7
79.5	86.6	89.5	+7.1	+10.0
20.5	13.4	10.5	+7.1	-10.0
56.0	64.2	70.8	+8.2	+14.8
44.0	35.8	29.2	-8.2	-14.8
16.2	19.4	27.2	+3.2	+11.0
83.8	80.6	72.8	-3.2	-11.0

^a The column designation conforms to Table I.

TABLE III

Results of Determination of Secondary and Tertiary Alcohols in Mixtures on the Columns A, B and D^a

The column designation conforms to Table I.

Substance	Introduced %	Found, %			Difference, %		
		A	B	D	A	B	D
Mixture No 1							
Cyclopentanol	28.0	34.1	17.3	31.3	+6.1	-10.7	+3.3
Cyclohexanol	22.7	17.9	21.7	28.9	-4.8	-1.0	+6.2
2-Methyl-2-heptanol	33.2	26.4	31.5	19.6	-6.8	-1.7	-13.6
3-Octanol	16.1	18.4	28.4	19.6	+2.3	+12.3	+3.5
Mixture No 2							
Cyclopentanol	7.1	6.7	5.8	5.7	-0.4	-1.3	-1.4
Cyclohexanol	20.4	22.5	13.3	16.4	+2.1	-7.1	-4.0
2-Methyl-2-heptanol	28.5	26.3	35.3	32.5	-2.2	+6.8	+4.0
3-Octanol	44.0	44.0	47.6	45.4	0.0	+3.6	+1.4

how the various types of ethylenes react with a methanolic solution of mercury(II) acetate, we aimed also to compare this reactivity in aqueous-tetrahydrofuran solutions.

EXPERIMENTAL

The gas chromatography (GC) analyses were performed on an apparatus Chrom IV with an ionization detector (FID) using nitrogen as the carrier gas. The columns used are described in Table I. The carriers as well as the stationary phases were commercial products of Lachema. Brno. The preparation of the alcohols used for the preparation of the olefins and also employed as the GC standards has been described elsewhere^{1-3,16}. A mixture of octalines containing from 80% the Δ 9,10 isomer was prepared by dehydration of β -decalols with a mixture of phosphoric acid and phosphorus pentoxide¹⁷. The content mentioned was found by GLC, using Δ 9,10-octaline as the standard; the latter was isolated *via* the crystalline chloronitroso derivative¹⁸.

The accuracy of determination of the percent contents of alcohols and olefins in a mixture after the OM-DM of the olefins was checked with a mixture of 6-tridecene and 7-tridecanol on Apiezon and Carbowax columns (Table II). The Apiezon column is seen to give results with a lower error ($\pm 8\%$) than the Carbowax column ($\pm 15\%$). When one of the components was concentrated to 10%, the errors were as low as $\pm 4\%$. In a next test a mixture of secondary and tertiary alcohols was analysed in the same manner and the best results were obtained with Apiezon L ($\pm 7\%$) (Table III). The conversion of the secondary and tertiary alcohols to the

TABLE IV
Results of Determination of Alcohols as the Acetates
The column A (Table I) was used; the analyses were performed at 105°C, 0.36 atm N₂.

Substance	Introduced %	Found %	Difference %
Mixture No 1			
Cyclopentanol	28.0	26.0	-2.0
Cyclohexanol	22.7	15.8	-6.9
2-Methyl-2-heptanol	33.2	28.1 ^a	-5.1
3-Octanol	16.1	20.6	+4.5
Mixture No 2			
Cyclopentanol	7.1	4.3	-2.8
Cyclohexanol	20.4	11.4	-9.0
2-Methyl-2-heptanol	28.5	26.2 ^b	-2.3
3-Octanol	44.0	53.5	+9.5

^a 8% alcohol remained unacetyled, its area was added to that of the acetate; ^b 3.8% alcohol remained unacetyled.

acetates was applied in some cases for the identification of their peaks. The conversion of the secondary alcohols by the procedure¹⁹ proceeded quantitatively, the tertiary alcohols, however, did not react completely. According to the analysis on Apiezon L (Table IV) the highest error amounted to $\pm 9\%$. Still, for a qualitative detection of the alcohols in the GC analysis of rich mixtures during the OM-DM of pyrolysis gasoline, the acetylation was convenient. On Apiezon L the acetate exhibited longer retention times than the alcohols, on Carbowax 6000 the reverse was true.

OM-DM of 1-undecene^{10,12}. 30 ml of tetrahydrofuran was added to 3.2 g (10 mmol) of mercury(II) acetate in 10 ml of water; the mixture turned yellow. 1.5 g (10 mmol) of 1-undecene was then added. The yellow colouration disappeared in 2.25 minutes. After 30 minutes of stirring the oxymercuration was interrupted by adding 10 ml of 3M-NaOH; 10 ml of 0.5M-NaBH₄ dissolved in 3M-NaOH was added and the mixture was stirred for additional 30 minutes. After salting out with potassium carbonate the tetrahydrofuran layer was separated and the aqueous phase was extracted with 3 × 25 ml of tetrahydrofuran. The tetrahydrofuran solution was dried with potassium carbonate and concentrated by distillation. The residue was analyzed (Table V).

OM-DM of a mixture of 2-methyl-1-heptene and 2-methyl-2-heptene in the presence of heptane and benzene. 1.42 g of this mixture was added to 4.07 g (12.65 mmol) of mercury(II) acetate dissolved in 12 ml of water and 36 ml of tetrahydrofuran. The yellow colour did not disappear after 3 h; the oxymercuration was stopped by adding 12 ml of 3M-NaOH, and the mixture was reduced with 12 ml of 0.5M-NaBH₄ in 3M-NaOH for 30 minutes. The further procedure was as in the previous experiments. The distillation residue was analyzed by GC on Carbowax (Column B). Introduced: 35% heptane, 46.1% benzene, 18.9% 2-methyl-1-heptene + 2-methyl-2-heptene; found: 29.5% heptane, 46.7% benzene, 0% 2-methyl-1-heptene + 2-methyl-2-heptene, 24.0% 2-methyl-2-heptanol.

The distillation of the pyrolysis gasoline was carried out on a distillation column (length 35 cm, diam. 1.4 cm) filled with fine tubes from a stainless gauze and heated by a heating jacket. The reflux ratio was 1 : 8. The receiver was cooled down to -60°C . An additional flask was inserted to catch the noncondensed vapours. 160 g of the pyrolysis gasoline taken from a pyrolysis unit of Chemical Works in Záluží was stabilized with an addition of 0.03% 1-hydroxy-2,6-bis(1',1'-dimethylethyl)-4-methylbenzene (Topanol) and then was distilled. The fractions were obtained as follows: 1. b.p. 24–29°C (5.5 g), 2. 29–35° (5.5 g), 3. 37–40°C, (3.9 g), 4. 40–43°C (3.6 g). The total of 14 fractions were taken, the last had the b.p. 107–111°C. As a gradual decomposition took place at this temperature and atmospheric pressure, the residue (28%) was fractionated at 45 Torr.

OM-DM of the 2nd distillation fraction (b.p. 29–35°C) of the pyrolysis gasoline. 5.4 g of the fraction was added in a sealed thin-walled ampoule to a mixture of 48.7 g of mercury(II) acetate, 126 ml of water, and 126 ml of tetrahydrofuran in a 1 l bottle; the bottle was closed with a stopper and the mixture was shaken for 55 h. The reaction was interrupted by adding 150 ml of 3M-NaOH and 150 ml of 0.5M-NaBH₄ in 3M-NaOH. 350 g of anhydrous K₂CO₃ was applied for the salting out. The tetrahydrofuran layer was separated, the aqueous phase was extracted with 4.80 ml of tetrahydrofuran for 44 h and the extracts were dried with K₂CO₃ and concentrated on the separation column used before for the pyrolysis gasoline distillation. The distillation residue, 6.41 g, contained 36% tetrahydrofuran (GLC on Carbowax 6000).

OM-DM of the 1st and the 4th distillation fractions was performed in an analogous manner. The chromatogram of the alcohol mixture prepared by the OM-DM from the 4th fraction shown in Fig. 1. The results of analyses are given in Table VI.

TABLE V

Conversion of Olefins to Alcohols

The time period to the vanishing of the yellow colouration of the reaction mixture t_1 and the total duration of the oxymercuration t_2 were followed; the columns A with Apiezon and B with Carbowax (Table I) were used; the vol. ratio of tetrahydrofuran and water was 3 : 1; the substances were identified by means of standards.

t_1 min	t_2 min	Products, t_R , min			
		Apiezon	%	Carbowax	%
1-Heptene					
2.61	20	1-heptene (4.5)	0.0	1-heptene (1.25)	0.0
		unknown (7.75)	2.5	unknown (3.12)	1.8
		2-heptanol (15.12)	97.5	unknown (5.87)	2.9
				2-heptanol (8.25)	95.1
1-Undecene					
2.25	30	1-undecene (6.50)	3.9	1-undecene (4.25)	1.7
		2-undecanol (23.75)	96.1	unknown (6.50)	3.0
				2-undecanol (8.62)	95.3
2-Methyl-1-hexene^a					
0.50	15	2-methyl-1-hexene (5.25)	0.0	2-methyl-1-hexene (3.5)	3.0
		2-methyl-2-hexanol (8.62)	100.0	2-methyl-2-hexanol (5.25)	97.0
2-Methyl-1-hexene + 2-methyl-2-hexene					
4.40	60	the starting olefins (5.25)	0.0	the starting olefins (0.75)	4.4
		2-methyl-2-hexanol (8.62)	100.0	2-methyl-2-hexanol (6.50)	95.6
2-Methyl-1-heptene + 2-methyl-2-heptene					
6.85	70	the starting olefins (7.75)	0.0	the starting olefins (0.75)	3.0
		unknown	5.8	unknown (1.75)	1.1
				unknown (2.50)	4.8
				unknown (3.25)	0.8
		2-methyl-2-heptanol (13.50)	94.2	2-methyl-2-heptanol (5.50)	90.3
2-Methyl-1-decene + 2-methyl-2-decene					
20	540	the starting olefins (3.75)	3.0	the starting olefins (0.75)	3.3
		2-methyl-2-decanol (7.25)	97.0	2-methyl-2-decanol (4.12)	96.6
3-Methyl-2-hexene + 3-methyl-3-hexene					
15	75	the starting olefins (5.50)	0.0	the starting olefins (1.00)	0.0
		3-methyl-3-hexanol (9.50)	94.6	unknown (2.62)	3.2
		unknown (12.37)	5.4	unknown (3.50)	4.5
				3-methyl-3-hexanol (4.00)	92.3

^a Tetrahydrofuran: water ratio 1 : 1 (vol.).

TABLE VI

Chromatography of Alcohol Mixtures Prepared by Oxymercuration–Demercuration of Distillation Fractions of Pyrolysis Gasoline

The column G (Table I) was used.

% Peak area	Retention time, min		Products
	alcohol	acetate	
Fraction b.p. 24–29°C			
58.7	8.50	8.50	2-butanol ^{a,b} , 2-methyl-2-butanol ^b
11.2	9.50	8.87	methyltetrahydropyran ^{b,c} , unidentified alcohol ^b
4.0	10.75	9.50	
3.6	12.25	11.25	
15.0	13.90	12.50	2-pentanol ^{a,b} , unidentified alcohol ^b
7.6	16.87	15.00	m. wt. 102; unidentified unsatd. alcohol ^b
Fraction b.p. 29–35°C			
0.4	6.50	5.75	
11.0	8.50	7.87	2-butanol ^{a,b} , methyltetrahydropyran ^b
	9.50	8.25	
4.0	10.75	9.50	
4.8	12.00	11.00	
57.0	13.00	12.50	3-pentanol ^a
10.8	14.00	12.50	2-pentanol ^{a,b}
4.3	15.75	17.75	4-methyl-2-pentanol ^b
Traces	16.50	31.75	3,3-dimethyl-2-butanol ^b
4.3	18.00	—	
3.3	37.50	—	C ₇ alcohol ^b
Fraction b.p. 40–43.5°C			
10.2	8.12	8.50	2-methyl-2-butanol ^b , 2-butanol ^{a,b}
73.7	8.87	9.50	2-pentanol ^b
3.6	13.75	11.25	m. wt. 102, 4-methyl-2-pentanol ^b
2.3	15.75	12.50	3,3-dimethyl-2-butanol ^b
10.2	37.25	15.00	unidentified alcohol C ₇

^a Determined by comparing the retention time with those of standards, *viz.*: 2-methyl-2-propanol 5.00, 5.87; 2-propanol 5.75, 5.87; 2-methyl-2-butanol 8.50, 9.75; 2-butanol 8.75, 8.25; 3-pentanol 13.00, 12.25; 2-pentanol 13.75, 12.75 min; ^b identified by mass spectrometry; the mixture was separated to components on the GC column H (Table I) at programmed temperature (t_{init} 30°C; 5°C/min. He flow rate 10 ml/min) and run on a mass spectrometer LKB 9000; ^c the formation of 2-methyltetrahydropyran during OD-DM of 1,2-epoxy-5-hexen-5-ol has been described²².

RESULTS AND DISCUSSION

Asymmetrically mono-, di- and trisubstituted and symmetrically *cis* and *trans* disubstituted ethylenes have been detected^{6,20} in pyrolysis gasoline. As to dienes, both conjugated and nonconjugated, conjugated substituted, and cyclic nonconjugated ones have been found.

Monosubstituted ethylenes: 1-heptene and 1-undecene react with methanolic solutions of mercury(II) acetate most rapidly; this applies also to the oxymercuration in aqueous–tetrahydrofuran solutions. We determined the oxymercuration rate by measuring the time elapsing between the addition of the olefin under study to the aqueous–tetrahydrofuran solution of mercury(II) acetate and the disappearing of the yellow colouration formed^{10–14}. (In some cases this colouration did not disappear at all or it changed to green). 1-Heptene and 1-undecene yielded almost quantitatively 2-heptanol and 2-undecanol, respectively (Table V). The side products amounted at most to 3%. The fact that in these cases exclusively alcohols with the hydroxy group at the second carbon atom are formed during the OM-DM has been proved by the authors of this method^{10–14}. We verified this with 2-heptanol, by comparing its GC, ¹H NMR, IR with an authentic chemical. 2-Methyl-1-hexene – an asymmetrically disubstituted ethylene – converted rapidly almost completely to 2-methyl-2-heptanol.

As we did not have always the individual olefins at our disposal, and we intend to apply the hydroxylation method to olefin mixtures, too, we tested the method also with mixtures of olefins formed on dehydration of secondary and tertiary alcohols. The mixtures of asymmetrically disubstituted and trisubstituted ethylenes with a methyl group at the second carbon atom, *viz.* 2-methyl-1-hexene + 2-methyl-2-hexene (Table V), 2-methyl-1-heptene + 2-methyl-2-heptene, and 2-methyl-1-decene + 2-methyl-2-decene afforded on the OM-DM the expected tertiary alcohols almost quantitatively. From a comparison of the duration of oxymercuration of these ethylenes the retarding effect of the alkyl group at the double bond is apparent; the bulkier the alkyl group, the slower course of the oxymercuration. In order to verify that the expected tertiary alcohol is formed solely, we compared the ¹H-NMR spectrum of 2-methyl-2-decanol prepared from acetone and octylmagnesium bromide with that of the alcohol obtained from the hydroxylation of a mixture of 2-methyl-1-decene and 2-methyl-2-decene. The two spectra were entirely identical. The mixture of the asymmetrically trisubstituted ethylenes: 3-methyl-2-hexene and 3-methyl-3-hexene converted to 3-methyl-3-hexanol with a good yield, too (Table V).

Symmetrically *trans*-disubstituted ethylenes reacted considerably more slowly than the asymmetrically mono-di-, and trisubstituted ethylenes as described above. Thus, *e.g.*, the oxymercuration of a mixture of 1-pentene and 2-pentene (with a predominating content of *trans*-2-pentene) proceeded quantitatively in 3 h and afforded 54% 2-pentanol and 41% 3-pentanol (Table VII). This hydroxylation has been reported¹⁰ for pure *trans*-2-pentene, which gave 54% 2- and 46% 3-pentanol, and for pure

TABLE VII

Conversion of Olefins to Alcohols

The time period to the vanishing of the yellow colouration of the reaction mixture t_1 and the total duration of the oxymercuration t_2 were followed; the columns A with Apiezon and B with Carbowax (Table I) were used; the vol. ratio of tetrahydrofuran and water was 3 : 1; the substances were identified by means of standards.

t_1 h	t_2 h	Products, t_R , min			
		Apiezon	%	Carbowax	%
2-Pentene + 1-pentene					
3	9	the starting olefins	0.0	unknown (8.50)	2.8
		2-pentanol (5.00)	99.0	unknown (9.50)	2.3
		unknown (7.25)	1.0	3-pentanol (13.0)	41.0
				2-pentanol (13.75)	53.9
3-Heptene					
11	12.5	3-heptene (2.25)	5.5	3-heptene (1.0)	1.5
		4-heptanol (10)	94.5	unknown (3.37)	12.9
				4-heptanol (6.75)	74.3
				unknown (7.75)	11.3
6-Tridecene					
∞	42	unknown (4.50)	2.0	6-tridecene (2.75)	2.5
		6-tridecene (5.75)	25.2	6-tridecene (3.50)	28.0
		7-tridecanol (13.50)	72.8	unknown (7.0)	1.9
				7-tridecanol (8.97)	67.6
Cyclopentene					
0.23	2	cyclopentene (3.00)	0.0	cyclopentene (2.00)	0.0
		cyclopentanol (6.62)	100.0	cyclopentanol (4.50)	100.0
Cyclohexene					
0.03	0.5	cyclohexene (3.75)	0.0	cyclohexene (2.75)	0.0
		cyclohexanol (17.00)	100.0	unknown (5.75)	1.7
				unknown (7.00)	1.1
				cyclohexanol (8.75)	95.8
				unknown (10.50)	1.5
2-Methyl-3-propyl-2-hexene ^a					
∞	18	2-methyl-3-propyl-2-hexene (4.0)	88.0	2-methyl-3-propyl-2-hexene (5.25)	91.4
		unknown (7.32) ^b	12.0	unknown (11.50) ^c	8.6

TABLE VII
(Continued)

t_1 h	t_2 h	Products, t_R , min			
		Apiezon	%	Carbowax	%
A mixture of octalines containing predominantly the Δ 9,10 isomer					
∞	20	the starting olefins (3.50, 4.25, 5.00)	83.9	the starting olefins (1.50, 3.50, 6.50)	77.1
		unknown (6.75)	7.8	unknown (8.25)	2.4
		unknown (8.00)	1.2	unknown (9.75)	16.4
		unknown (10.12)	3.9	unknown (12.15)	4.0
		unknown	3.1		

^a Ratio tetrahydrofuran: water 1 : 1 (vol.); ^b t_R of 2-methyl-3-propyl-2-hexanol 4.75, 5.50, 8.50 min;

^c 12.50 min.

cis-2-pentene, with the yield of 65% 2- and 35% 3-pentanol. Our result approaches that obtained with the *trans* isomer. 3-Heptene discoloured the oxymercuration reagent only after 11 h; only 5.5% starting olefins were found in the product, the main component being 4-heptanol. 6-Tridecene did not discolour the reagent even after 42 h and the reaction mixture contained as much as 25% unreacted *trans*-disubstituted ethylene. The main reaction product was 7-tridecanol, as proved also by the mixed melting point. In accordance with the paper¹⁰, symmetrically disubstituted ethylenic bonds in the cycloolefins: cyclopentene and cyclohexene reacted in the OM-DM rapidly and quantitatively with the formation of cyclopentanol and cyclohexanol, respectively, with a very low content of side products.

The symmetrically tetrasubstituted ethylenic bonds in 2-methyl-3-propyl-2-hexene remained virtually intact during the OM-DM — it reacted only from 10%. The expected 2-methyl-3-propyl-3-hexanol was not detected by GLC in the OM-DM products. This is in accordance with our previous results¹⁵: the tetrasubstituted ethylene: Δ 9,10-octahydronaphthalene was nonreactive, too, in a methanolic solution of mercury(II) acetate. During the oxymercuration of a mixture of octalines with a predominant content of the Δ 9,10-isomer in an aqueous-tetrahydrofuran solution, the yellow colour did not disappear even after 20 h and only 16% entered the reaction during that period (Table VII).

In order to verify that the presence of paraffinic and aromatic hydrocarbons does not affect the course of the OM DM, we added benzene and heptane to a mixture of 2-methyl-1-heptene and 2-methyl-2-heptene. The olefins converted quantitatively to 2-methyl-2-heptanol. In another experiment we extended the above mixture by 1-heptene, cyclopentene, and cyclohexene. After its OM-DM (Table VIII) we eva-

luated the contents of the alcohols formed with respect to those of the starting olefins: the differences were $\pm 5\%$ when diethylene glycolsuccinate was used, on Apiezon L and on Carbowax 6000 they were ± 7.5 .

In the pyrolysis gasoline sample analyzed we determined the ethylenic bonds with a methanolic solution of mercury(II) acetate²¹. Their content found corresponded to 56% octene. The highest concentrations of the ethylenic bonds were found in the

TABLE VIII

Determination of the Olefins of a Mixture Containing 60.97% Olefins and 39.03% Heptane and Benzene by Oxymercuration-Demercuration and Chromatography on the Columns A, B, and D^a

Olefin	Introduced, % of the olefinic part	Found ^b , %/Difference, %		
		A	B	D
1-Heptene	16.7	18.4/+1.7	14.2/-2.5	17.3/+0.6
2-Methyl-1-heptene	32.6	35.6/+3.0	38.3/+5.7	36.9/+4.3
2-Methyl-2-heptene				
Cyclopentene	27.4	31.8/+4.4	31.8/+4.4	27.3/-0.1
Cyclohexene	23.3	15.8/-7.5	15.8/-7.5	18.4/-4.9

^a The column designation conforms to Table I; ^b % of the olefinic part.

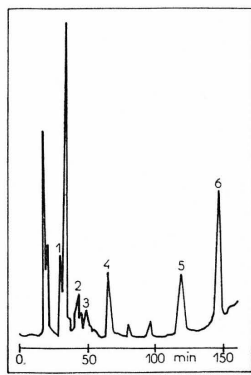


FIG. 1

Chromatogram of the Alcohols Prepared by Oxymercuration-Demercuration from a Fraction of Pyrolysis Gasoline, b.p. 40 to 43.5°C

The following compounds were identified by mass spectrometry: 1 2-methyl-2-butanol and 2-butanol; 2 2-pentanol; 3 4-methyl-2-pentanol; 4 3,3-dimethyl-2-butanol; 5 unidentified alcohol C₇; 6 unidentified compound. The column H (Table I) was used at programmed temperature, the conditions are given in Table VI.

fractions b.p. 24–60°C and the lowest in the fractions b.p. 60–100°C, a somewhat higher content was found in the higher-boiling part, up to m.p. 180°C. We analyzed the alcohol mixtures from these fractions by isothermal GLC as well as by GLC with programmed temperature with a simultaneous running of the mass spectra of the individual peaks. The mass spectrometer was, however, equipped with a less efficient chromatographic column, and therefore two compounds appeared occasionally in one peak (Fig. 1). We acetylated the alcohol mixtures, too. From the first fractions of the pyrolysis gasoline we prepared so far six alcohols (Table VI), which indicate the presence of the following olefins: 1-butene + 2-butene, 1-pentene + 2-pentene, 2-methyl-1-butene + 2-methyl-2-butene, 4-methyl-1-pentene + 4-methyl-2-pentene, and 3,3-dimethyl-1-butene. Except for the last compound, these olefin mixtures have been found in pyrolysis gasoline recently^{6,20}.

The mass spectra were measured and evaluated by Dr P. Zachař, the NMR spectra by Dr M. Hájek, some technical works were done by Mrs M. Kupková. The IR spectra were measured by Dr E. Janečková and Dr A. Kohoutová, Central Laboratories of the Institute.

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