

## Capillary column gas chromatography of C<sub>6</sub>-C<sub>11</sub> aromatic compounds

### Synthesis of selected isomers for identification purposes

This work extends the gas chromatography of C<sub>6</sub>-C<sub>10</sub> alkylbenzenes to include C<sub>11</sub> alkylbenzenes, styrenes, indene, indan, tetralin, and naphthalene. Previous studies of aromatic compounds include only the C<sub>6</sub>-C<sub>10</sub> alkylbenzenes<sup>1-4</sup>. Capillary columns and temperature programming are used as these techniques are best for complex wide boiling range mixtures such as C<sub>6</sub>-C<sub>11</sub> aromatics. Mixtures of selected C<sub>10</sub> and C<sub>11</sub> alkylbenzene isomers are synthesized and used for identification purposes. The initial identification of these isomer mixtures using mechanistic and kinetic considerations is described.

### Experimental

*Gas chromatography.* A 300-ft. by 0.02-in. I.D. Type 347 stainless steel column was coated by passing a 10% solution of Ucon LB550X dissolved in methylene chloride through the column with a pressure of 20 p.s.i.g. The column has been used for approximately two years without noticeable deterioration. All data were obtained with a Perkin-Elmer Model 800 gas chromatograph. The experimental conditions are:

- (1) Injector temperature 200° minimum
- (2) Detector temperature 130° minimum
- (3) Column temperature 60-130° at 1°/min
- (4) Inlet pressure 20 p.s.i.g.
- (5) Sample size 1-5 μl
- (6) Split ratio determined by No. 25 syringe needle
- (7) Recorder speed 3 in./min (4 in./min for better accuracy on early peaks)
- (8) Electrometer attenuation 5-100 depending on sensitivity required.

*Alkylbenzene synthesis.* Isomeric C<sub>10</sub> and C<sub>11</sub> alkylbenzenes were prepared for identification purposes by disproportionation of 1-methyl-2-ethylbenzene (1M2EB). The 1M2EB had a purity of 99.8% according to gas chromatography. The disproportionation was run in a 1/4 in. O.D. stainless steel tube containing 0.5 ml silica-alumina cracking catalyst containing 10% alumina. The catalyst mesh size was 100/200. Experiments were made at atmospheric pressure and 400°. The reaction was run with hydrogen dilution using a mole ratio of hydrogen to methylethylbenzene of 3:1. Liquid feed rates were 4, 8 and 16 ml/h. The corresponding hydrogen flow rates were 32, 64 and 128 STP ml/min. The reaction product was collected in an acetone-dry ice-cooled condenser. Reaction periods were 65 min.

### Discussion

A chromatogram of a C<sub>6</sub>-C<sub>11</sub> aromatic blend is illustrated in Fig. 1. Peak identifications are given in Table I. The small unidentified peaks between toluene and ethylbenzene are paraffinic compounds present as impurities. The unidentified peaks eluting at the end are C<sub>11</sub> alkylbenzenes, styrene, indan and/or indene homologues. Four pairs are at least partially resolved: 1M4EB and 1M3EB; 1M2EB and tBB; 1M4nPB and 14DEB; 1234TeMB and 1M25DEB. The latter pair includes a C<sub>11</sub> alkylbenzene and more overlap is expected as other C<sub>11</sub> isomers are identified.

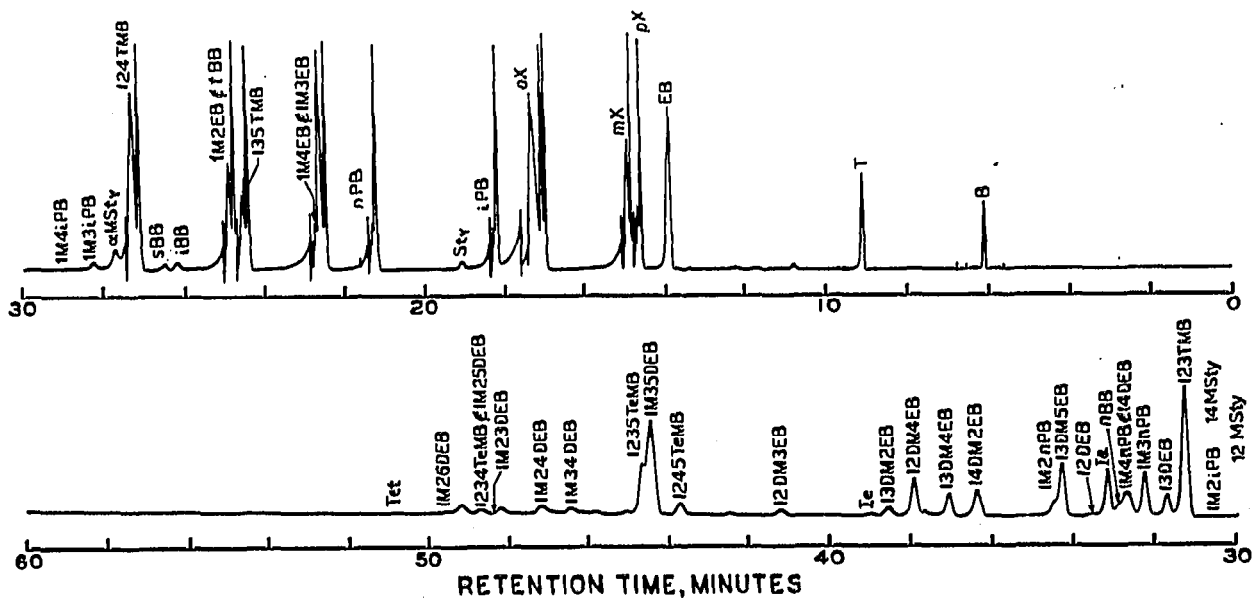


Fig. 1. Chromatogram of  $C_6-C_{11}$  aromatic blend. For abbreviations, see Table I.

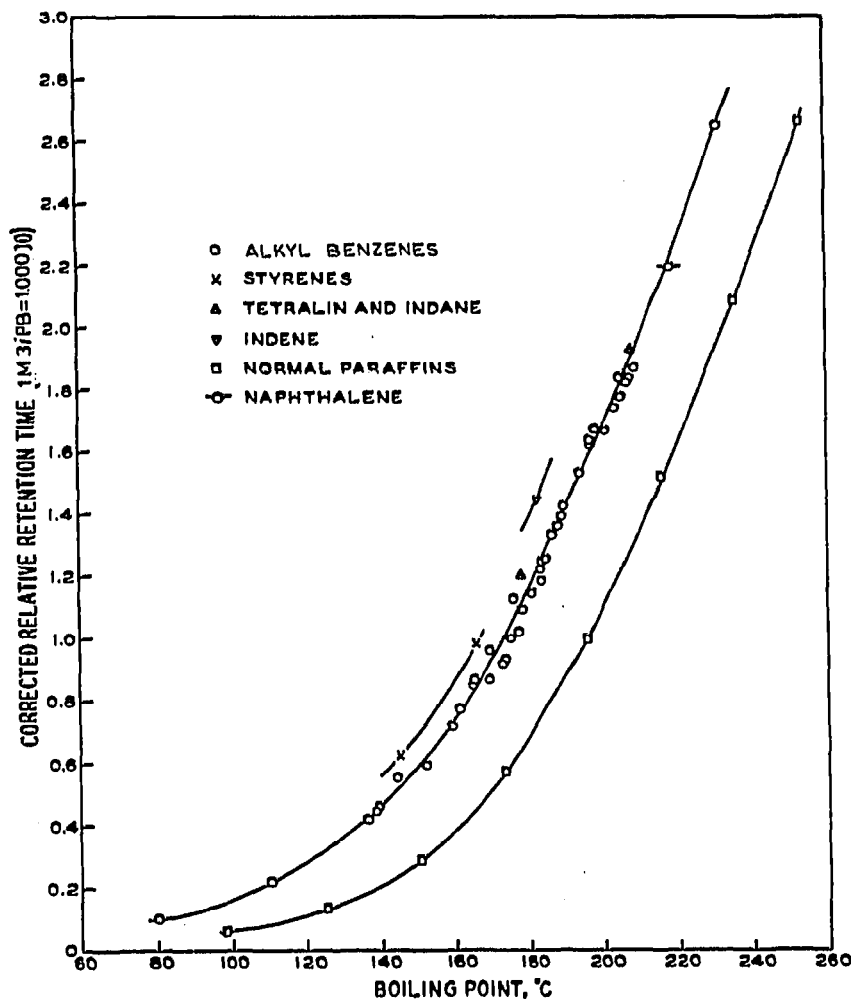


Fig. 2. Retention data *versus* boiling point. For abbreviations, see Table I.

TABLE I  
SUMMARY OF RETENTION DATA

Compound name	Abbreviation	Boiling point (°C)	Retention time (min)	Adjusted relative retention time	Retention index
Methane			3.66		100
Benzene	B	80.100	6.12	0.100	753
Toluene	T	110.625	9.06	0.220	856
Ethylbenzene	EB	136.186	13.89	0.417	948
<i>p</i> -Xylene	<i>p</i> X	138.351	14.62	0.446	955
<i>m</i> -Xylene	<i>m</i> X	139.103	14.92	0.458	959
<i>o</i> -Xylene	<i>o</i> X	144.411	17.22	0.552	992
Isopropylbenzene	iPB	152.392	18.27	0.595	1005
Styrene	Sty	145.14	19.02	0.625	1012
<i>n</i> -Propylbenzene	<i>n</i> PB	159.2	21.29	0.718	1034
1-Methyl-4-ethylbenzene	1M4EB	161.989	22.55	0.770	1046
1-Methyl-3-ethylbenzene	1M3EB	161.305			
1,3,5-Trimethylbenzene	135TMB	164.716	24.50	0.850	1065
1-Methyl-2-ethylbenzene	1M2EB	165.153			
<i>tert.</i> -Butylbenzene	tBB	169.119	24.88	0.865	1069
Isobutylbenzene	iBB	172.759			
<i>sec.</i> -Butylbenzene	sBB	173.305	26.10	0.915	1080
1,2,4-Trimethylbenzene	124TMB	169.351	26.46	0.929	1084
$\alpha$ -Methylstyrene	$\alpha$ MSty	165.5	27.20	0.958	1091
1-Methyl-3-isopropylbenzene	1M3iPB	175.05	27.68	0.978	1095
1-Methyl-4-isopropylbenzene	1M4iPB	177.10	28.20	1.000	1100
1-Methyl-2-isopropylbenzene	1M2iPB	178.15	28.62	1.017	1104
1,2,3-Trimethylbenzene	123TMB	176.084	30.50	1.093	1118
1,3-Diethylbenzene	13DEB	181.102	31.25	1.122	1123
1-Methyl-3- <i>n</i> -propylbenzene	1M3 <i>n</i> PB	181.98	31.70	1.142	1127
1-Methyl-4- <i>n</i> -propylbenzene	1M4 <i>n</i> PB	183.38	31.70	1.142	1127
1,4-Diethylbenzene	14DEB	183.752	32.25	1.164	1131
<i>n</i> -Butylbenzene	<i>n</i> BB	183.270	32.70	1.182	1135
Indan	Ia	177.82			
1,2-Diethylbenzene	12DEB	183.423	32.85	1.188	1136
1,3-Dimethyl-5-ethylbenzene	13DM5EB	183.58	33.15	1.200	1138
1-Methyl-2- <i>n</i> -propylbenzene	1M2 <i>n</i> PB	184.93	33.60	1.220	1142
1,4-Dimethyl-2-ethylbenzene	14DM2EB	186.83	34.25	1.246	1147
1,3-Dimethyl-4-ethylbenzene	13DM4EB	188.20	34.45	1.254	1148
Unknown			36.40	1.333	1163
1,2-Dimethyl-4-ethylbenzene	12DM4EB	189.48	37.05	1.360	1168
1,3-Dimethyl-2-ethylbenzene	13DM2EB	190.01	37.65	1.383	1172
Indene	Ie	182.44	37.80	1.390	1174
1,2-Dimethyl-3-ethylbenzene	12DM3EB	193.91	38.60	1.422	1180
Unknown			39.00	1.440	1183
1,2,4,5-Tetramethylbenzene	1245TeMB	196.80	41.20	1.530	1202
1-Methyl-3,5-diethylbenzene	1M35DEB	200.70	42.45	1.580	1211
1,2,3,5-Tetramethylbenzene	1235TeMB	198.00	43.75	1.633	1220
Unknown			44.45	1.662	1225
Unknown			44.65	1.670	1227
Unknown			45.05	1.683	1229
Unknown			45.80	1.718	1235
1-Methyl-3,4-diethylbenzene	1M34DEB	203.6	46.40	1.740	1239
1-Methyl-2,4-diethylbenzene	1M24DEB	205.0	47.20	1.773	1245
Unknown			48.25	1.817	1253
1-Methyl-2,3-diethylbenzene	1M23DEB	206.6	48.40	1.821	1253
1,2,3,4-Tetramethylbenzene	1234TeMB	205.04	48.75	1.837	1256
1-Methyl-2,5-diethylbenzene	1M25DEB	207.1			
Unknown			49.20	1.857	1260

(continued on p. 265)

TABLE I (continued)

Compound name	Abbreviation	Boiling point (°C)	Retention time (min)	Adjusted relative retention time	Retention index
1-Methyl-2,6-diethylbenzene	1M26DEB	208.8	49.60	1.870	1262
Tetralin	Tet	207.6	51.00	1.927	1272
Naphthalene	Naph	218.0	57.40	2.194	1319
<i>n</i> -Heptane	<i>n</i> C <sub>7</sub>	98.4	1.51	0.0615	700
<i>n</i> -Octane	<i>n</i> C <sub>8</sub>	125.7	3.30	0.134	800
<i>n</i> -Nonane	<i>n</i> C <sub>9</sub>	150.8	7.09	0.288	900
<i>n</i> -Decane	<i>n</i> C <sub>10</sub>	174.1	14.14	0.576	1000
<i>n</i> -Undecane	<i>n</i> C <sub>11</sub>	195.9	24.49	0.998	1100
<i>n</i> -Dodecane	<i>n</i> C <sub>12</sub>	216.3	37.34	1.520	1200
<i>n</i> -Tridecane	<i>n</i> C <sub>13</sub>	235.5	51.34	2.085	1300
<i>n</i> -Tetradecane	<i>n</i> C <sub>14</sub>	253.5	65.44	2.660	1400

TABLE II

DISPROPORTIONATION OF 1-METHYL-2-ETHYLBENZENE OVER SILICA-ALUMINA CRACKING CATALYST AT 400°

Experiment number	1	2	3
Liquid hourly space velocity ( $h^{-1}$ )	32	16	8
Calculated residence time (sec)	0.07	0.14	0.29
Product composition (mole %)*			
Unreacted 1-methyl-2-ethylbenzene	90.10	84.10	69.31
1-Methyl 3- and 4-ethylbenzenes	9.24	14.88	29.06
Toluene	0.40	0.62	0.86
Ethylbenzene	0.02	0.03	0.07
Total dimethylethylbenzenes	0.02	0.03	0.07
Total methyldiethylbenzenes	0.15	0.25	0.54
Other**	0.07	0.08	0.09
Total	100.00	100.00	100.00
Isomer distribution (mole %)			
1,2-Dimethyl-3-ethylbenzene	4.4	2.9	2.9
1,2-Dimethyl-4-ethylbenzene	5.4	7.7	24.3
1,3-Dimethyl-2-ethylbenzene	2.9	3.8	11.8
1,3-Dimethyl-4-ethylbenzene	34.3	29.8	3.0
1,3-Dimethyl-5-ethylbenzene	13.2	18.2	25.4
1,4-Dimethyl-2-ethylbenzene	39.9	37.6	32.6
1-Methyl-2,4-diethylbenzene	34.0	30.8	25.7
1-Methyl-2,5-diethylbenzene	37.3	32.2	28.0
1-Methyl-3,4-diethylbenzene	8.3	9.4	10.5
1-Methyl-3,5-diethylbenzene	20.4	27.6	35.8

\* Analysis of liquid product collected during 65-min experiments.

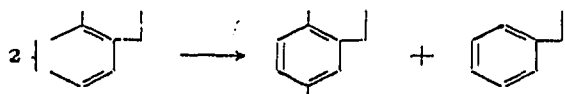
\*\* Benzene, xylenes, diethylbenzenes, and unidentified C<sub>12</sub> and higher secondary reaction products.

A plot of retention time *versus* boiling point is shown in Fig. 2. The alkylbenzenes group forms a single curve along with tetralin and indan. Styrenes and indenenes are retarded relative to the alkylbenzenes. More data are required to confirm this trend; but if it persists, it will aid in compound identification. The normal paraffin gives a similar correlation and is accelerated relative to aromatic compounds of corresponding volatility. The deviation from linearity in the lower part of the retention data plot is due to the fact that the conditions in this region are intermittent between isothermal and ideal temperature-programmed operation. The correlation of retention time and boiling point is nearly linear for the higher boiling compounds which do not migrate significantly at the initial temperature.

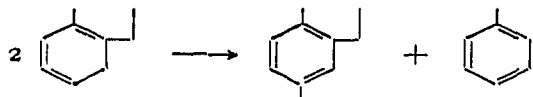
Peak identifications were made using pure compounds when available. Alkylbenzenes in the C<sub>9</sub>-C<sub>10</sub> range not available were identified using data from MCTAGGART AND MORTIMER<sup>2</sup>. Of the C<sub>11</sub> alkylbenzenes, only 1M35DEB was available in pure form.

Mixtures of additional isomers were synthesized by disproportionation of 1M2EB over silica-alumina catalyst. Evidence for 1,1-diphenylalkane intermediates in acid-catalyzed transalkylation was presented by STREITWIESER AND REIF<sup>5</sup>. Two types of disproportionation are possible with methylethylbenzenes:

A. Methyl transfer gives ethylbenzene and dimethylethylbenzenes.



B. Ethyl transfer gives methyldiethylbenzenes and toluene.



Conversions were kept below 1% disproportionation to avoid secondary reactions of the primary products. The only significant side reactions are isomerization of the 1M2EB to the *meta* and *para* isomer, and deethylation giving toluene and ethylene.

The results of the disproportionation reaction of 1M2EB are summarized in Table II. All six dimethylethylbenzenes were observed and were identified using pure compounds and the data of MCTAGGART AND MORTIMER<sup>2</sup>. The identifications agree with the above mechanism for disproportionation. The formation of two of the isomers (12DM4EB and 13DM5EB) requires isomerization before or after the disproportionation step. Data in Table II show that the yield of these compounds is increased significantly as the space velocity is decreased.

The data in Table II were used to help identify methyldiethylbenzenes. Only four of the six possible methyldiethylbenzenes were obtained from the disproportionation reaction. The formation of 1M34DEB and 1M35DEB require isomerization before or after the transalkylation step. The yield of these isomers increased with decreasing space velocity (Table II). 1M23DEB and 1M26DEB were not obtained because substitution of an ethyl group next to two other alkyl groups is sterically hindered. The methyldiethylbenzenes that were obtained were identified assuming a boiling point correlation similar to the dimethylethylbenzenes (Fig. 3) combined with the knowledge that the yield of 1M34DEB and 1M35DEB are space velocity dependent. The identification of 1M35DEB was confirmed by analyzing the pure material.

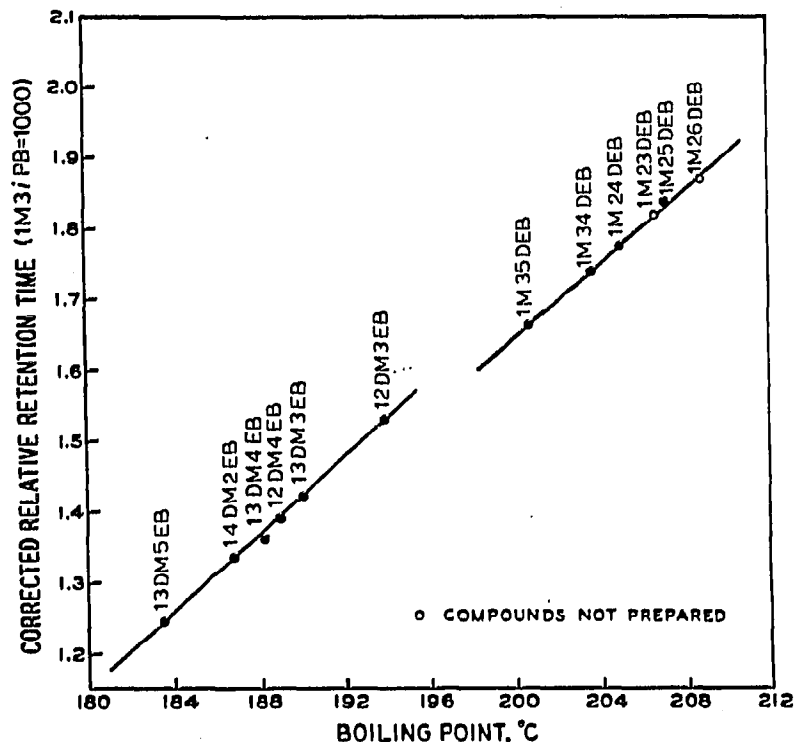


Fig. 3. Identification of methyl-diethylbenzenes in comparison with dimethylethylbenzenes. For abbreviations, see Table I.

### Conclusions

This technique of making mixtures of select isomers is potentially a powerful tool for the identification of other alkylbenzene isomers. Alkylation and isomerization are other reactions that yield mixtures of alkylbenzene isomers otherwise difficult to obtain. Information about mechanisms and kinetics can be used to help identify synthesized isomers.

Chevron Research Company, Richmond, Calif. (U.S.A.)

FREDERICK BAUMANN\*  
SIGMUND M. CSICSERY

- 1 R. L. MARTIN AND J. C. WINTERS, *Anal. Chem.*, 35 (1963) 1930.
- 2 N. G. McTAGGART AND J. V. MORTIMER, *J. Inst. Petrol.*, 50 (1964) 255.
- 3 H. MIYAKE AND M. MITOOKA, *Bull. Japan Petrol. Inst.*, 5 (1963) 58.
- 4 J. Q. WALKER AND D. L. AHLBERG, *Anal. Chem.*, 35 (1963) 2022.
- 5 A. STREITWIESER, JR. AND L. REIF, *J. Am. Chem. Soc.*, 82 (1960) 5003.

Received May 23rd, 1966

\* Varian-Aerograph, Walnut Creek, California.