

CHROM. 13,425

## Note

### Gas chromatography of some C<sub>13</sub>-C<sub>16</sub> alkylnaphthalenes on Bentone 34, silicone fluid DC 550 and Apiezon L phases

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(Received October 15th, 1980)

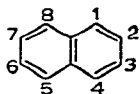
Gas chromatographic (GC) studies have been reported for a number of alkenylnaphthalenes<sup>1,2</sup>, for the monomethyl-, monoethyl- and dimethylnaphthalenes on a variety of stationary phases<sup>3-13</sup> and for methylethylnaphthalenes<sup>14</sup>, but there has been little investigation of GC characteristics of polymethylnaphthalenes<sup>3,5</sup> or of monoalkylnaphthalenes bearing propyl or larger groups. Nonetheless, there is considerable interest in such studies. From GC-mass spectrometry (MS) it was found<sup>9</sup> that cigarette smoke contains tri-, tetra-, and pentamethylnaphthalenes, but isomers were not resolved. Various mono-, di-, and polyalkylnaphthalenes were tentatively identified by retention data and spectral properties in a kerosene fraction<sup>11</sup> and in a low-temperature coal tar fraction<sup>3</sup>. Gonnord *et al.*<sup>7</sup> calculated retention data for all fourteen trimethylnaphthalene isomers on graphitized carbon black but measured data for only three isomers, while Engewald *et al.*<sup>13</sup> measured retention data for the same three trimethylnaphthalenes plus various propyl- and butylnaphthalenes with gas-liquid chromatography on glass capillaries as well as gas-solid chromatography on graphitized carbon black. We now report relative retention data for eighteen compounds in this series (Table I) on the stationary phases of Bentone 34, silicone fluid DC 550, and Apiezon L. Retention data for seven of these compounds on Bentone-Apiezon were also reported in a previous paper<sup>15</sup>. In our studies retention is given relative to naphthalene, which was run in admixture with a single alkylnaphthalene substrate in each experiment.

## EXPERIMENTAL

Naphthalene (reagent grade) was a commercial sample. All alkylnaphthalenes except No. 7 (a commercial sample) were available in purified form from previous research in our laboratory<sup>15-17</sup>. The apparatus and general procedure were as described before<sup>2</sup>. Three stationary phases, *viz.* 10% silicone fluid DC 550 on Chromosorb W (designated SW), 10% Bentone 34 on Chromosorb P (BP), and 10% Apiezon L on Chromosorb P (AP) were used<sup>2</sup>. Average retention values (reproducible to <1%) are given in Table I for a column of dimensions 2.4 m × 0.95 cm O.D.

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TABLE I

RELATIVE RETENTION ( $V_R$ ) OF MONO- AND POLYALKYLNAPHTHALENES AT 200°C $V_R$  relative to naphthalene (= 1.00).

No.	Substituent(s) on naphthalene	Literature datum	$V_R$			$V_R$ quotient, BP/AP
			SW	BP	AP	
1	1- <i>n</i> -C <sub>3</sub> H <sub>7</sub>	272.8*	2.66	2.79	3.07	0.91
2	2- <i>n</i> -C <sub>3</sub> H <sub>7</sub>	273.5*	2.65	3.11	3.16	0.98
3	1- <i>iso</i> -C <sub>3</sub> H <sub>7</sub>	267.8*	2.44	2.56	2.76	0.93
4	2- <i>iso</i> -C <sub>3</sub> H <sub>7</sub>	268.2*	2.30	2.61	2.70	0.97
5	1- <i>tert.</i> -C <sub>4</sub> H <sub>9</sub>	278.3*	3.25	3.06	3.73	0.82
6	2- <i>tert.</i> -C <sub>4</sub> H <sub>9</sub>	280.1*	2.88	2.93	3.46	0.85
7	1,2-(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>		3.85	4.28	4.57	0.94
8	1,2,3-(CH <sub>3</sub> ) <sub>3</sub>	1.53**	4.26	5.68	5.50	1.03
9	1,2,4-(CH <sub>3</sub> ) <sub>3</sub>	1.31**	3.83	5.26	5.17	1.02
10	1,2,7-(CH <sub>3</sub> ) <sub>3</sub>	2.28**	3.51	4.60	4.48	1.03
11	1,3,7-(CH <sub>3</sub> ) <sub>3</sub>	1.00***	3.06	5.38	3.85	1.40
12	1,4,5-(CH <sub>3</sub> ) <sub>3</sub>	1.60***	4.42	4.85	5.86	0.83
13	2,3,5-(CH <sub>3</sub> ) <sub>3</sub>	1.08***	3.56	5.89	4.56	1.29
14	2,3,6-(CH <sub>3</sub> ) <sub>3</sub>	1.17***	3.34	5.43	4.33	1.25
15	1,2,3,4-(CH <sub>3</sub> ) <sub>4</sub>		7.90	10.35	11.26	0.92
16	1,2,4,7-(CH <sub>3</sub> ) <sub>4</sub>		5.34	8.96	7.51	1.19
17	1,2,3,4,6-(CH <sub>3</sub> ) <sub>5</sub>		11.72	15.93	16.49	0.97
18	1,2,3,4,6,7-(CH <sub>3</sub> ) <sub>6</sub>		20.98	29.60	26.88	1.10

\* Normal boiling point, °C (see ref. 18).

\*\* Predicted  $V_R$ , relative to 11, for gas-solid chromatography on graphitized carbon black at 280°C (see ref. 7).\*\*\* Measured  $V_R$  for conditions above. To convert to naphthalene as a reference compound, multiply value given by 29.51.

## RESULTS AND DISCUSSION

Our data serve to complement and extend the chromatographic results reported by others for various mono-, di-, and polyalkylnaphthalenes, whereby relative retentions are interpretable (ideally) in terms of either volatility (*i.e.* boiling point progression) or adsorbability. This concept was clearly expounded by Frycka<sup>8</sup>, who noted that "conventional liquid phases" (*i.e.* relatively non-polarizing ones such as silicone and Apiezon) generally allow elution of C<sub>11</sub> and C<sub>12</sub> alkylnaphthalenes according to boiling point, graphitized carbon black as a stationary phase exhibits effects of steric hindrance and ring-substitution pattern<sup>13</sup> on adsorption of the substrate, and Bentone retains compounds through an interplay of these various properties<sup>2,8</sup>. A search of the literature produced apparently consistent data on boiling points of our substrates only in the monoalkylnaphthalene series, 1-6, (Table I). The retention values for all three stationary phases show nearly monotonic progressions with volatility except for 2-*tert.*-butylnaphthalene, which is eluted considerably sooner than expected. The shorter retention times of the isopropylnaphthalenes, as compared

to the *n*-propyl isomers, conform with observations on the effect of branching in alkyl chains found for butylnaphthalenes<sup>13</sup>. Moreover, the order of retention on AP of 6>2>1>4 also occurs with the stationary phases OV-1 and UCON LB 550 X<sup>13</sup>. Although retention times showed the order BP>AP>SW, the  $V_R$  quotient of BP/AP was less than 1 for all compounds 1-6, as well as for 1,2-diethylnaphthalene. In each of these seven cases the fractional value of the  $V_R$  quotient may reflect the effect of steric hindrance by the alkyl group(s) to flatwise adsorption of the naphthalene ring on to the aluminosilicate sheets of Bentone<sup>2</sup>.

For polymethylnaphthalenes one would expect volatility and relative retention to increase with increasing number of substituent groups,  $n$ <sup>17,19</sup>. Although there is considerable variation in  $V_R$  for isomers there is, indeed, a monotonic relationship between  $V_R$  and  $n$  for each of the three stationary phases. The order of retention 15>12>9>13>10>1 on AP agrees with that found on poly(ethylene glycol adipate)<sup>11</sup>; as does the order 13>14>11 on AP agree with those on OV-1<sup>13</sup>, UCON LB 550 X<sup>13</sup> and 25% Apiezon L on firebrick<sup>3</sup>.

$V_R$  quotients for the series 8-18 vary from 0.83 for 1,4,5-trimethylnaphthalene (12) to 1.40 for 1,3,7-trimethylnaphthalene (11). It is suggested that the low quotient for 12 results from distortion of the *peri* methyl groups out of the plane of the ring, with attendant steric hindrance to flatwise adsorption onto Bentone. A relatively low retention on Bentone was likewise reported for the *peri*-substituted 1,8-dimethylnaphthalene<sup>8</sup>. The low quotients for 8, 9, 10 and, especially, 15 imply that a 1,2-substitution pattern on the naphthalene ring may produce a similar, albeit smaller, distortion. Quotients for the homologous series 8, 15, 17 and 18 (see also 9 and 16) indicate that effects of the 1,2-pattern can be counteracted by additional methyl substituents in  $\beta$ -positions. In fact, the high values of the quotients for 11, 13 and 14 probably result from the preponderance of  $\beta$ -substituents therein. Comparison of the quotients for the trimethylnaphthalene isomers 8-14 with relative retentions on graphitized carbon black, as measured or predicted by others<sup>7,13</sup> (see Table I), shows no apparent direct relationship. While this lack of correlation is somewhat surprising it is consistent with the observations of Frycka<sup>8</sup> that Bentone and graphitized carbon black differ in the natures of their adsorption characteristics.

## CONCLUSIONS

GC retention data for alkylnaphthalenes in the C<sub>13</sub>-C<sub>16</sub> range with Bentone 34 on Chromosorb P at 200°C are dependent both on volatility (as measured with Apiezon L on the same support) and adsorbability of the substrate molecules. With Bentone the alkyl substituent(s) may serve either to increase or to decrease relative retention (as compared to the situation with Apiezon as a stationary phase) depending on the nature(s) and position(s) of the substituent(s) on the naphthalene ring. Data for silicone fluid DC 550 (on Chromosorb W) as the stationary phase generally are consistent with those for Apiezon, but the latter shows greater discrimination especially in retention of polymethylnaphthalenes.

## ACKNOWLEDGEMENTS

This study was supported by research grants No. CA-5969 from the National

Cancer Institute and No. GM 12730 from the National Institute of General Medical Sciences, U.S. Public Health Service. K. C. B. thanks the National Science Foundation for awarding him an Undergraduate Research Participantship during this investigation.

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