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RELATIVE RETENTIONS OF C_1–C_{15} ALKYL- AND ALKENYLPYRIDINES OVER DIFFERENT COLUMNS AND AT VARIOUS TEMPERATURES

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SUMMARY

The relative retentions of fifty 2- and 4-alkyl- and alkenylpyridines were determined over four different gas–liquid chromatographic columns and at various temperatures. The relation between the structure of the pyridines and their relative retention times is discussed.

INTRODUCTION

An extensive study of catalytic alkylation and alkenylation of alkylpyridines carried out in our laboratory[1–8] required reliable methods for the analysis of complex reaction mixtures. Gas chromatography was found to be a satisfactory tool for that purpose.

In the early studies of the ethylation of alkylpyridines[2,3], columns recommended by DECORA AND DRINNEEN[9] were used. The study of butenylation of alkylpyridines, however, required columns enabling quantitative determination of compounds having a wide boiling range and containing also compounds composed of double-bond isomers.

There are several papers describing various columns for gas–liquid chromatography of various nitrogen ring compounds including picolines and ethylpyridines and their derivatives[8–17]. The most extensive studies were those of FITZGERALD[10], JANÁK AND HŘIVNÁČ[11], and DECORA AND DRINNEEN[9]. It was reported that the separation of picolines can be achieved on columns containing glycerol[12,13]. Derivatives of pyridines and of other heterocyclic bases can be analyzed on polyethylene glycol adipate[14,15] and on Reoplex 400 (ref. 11). Dodecylphthalate[16], Silicone Oil DC-703 (ref. 9), squalene[9], and Apiezon L[9,17] were also recommended, and the last three were reported to give good selectivity and peak symmetry.

Columns containing the following liquid phases have been tested presently for the separation of substituted pyridines: Silicone Gum GE-SE-30 and GE-SE-52, Silicone 550, LAC-720, UCON 75, Carbowax 20M, Carbowax 750, Apiezon L, Reoplex 400, and Versamide 900.

EXPERIMENTAL

An F&M Model 720 dual-column gas chromatograph with a thermal conductivity detector was used. Liquid samples of 2–3 μl were injected by means of a Hamilton microliter syringe and all the determinations were made at constant temperatures. Helium was used as the carrier gas, at a flow rate of 80–100 ml/min and an inlet pressure of 35 p.s.i.; the flow rate was measured at the outlet using a bubble flowmeter. The columns are listed in Table I. They were made from 1/4 in. O.D. copper tubes bent into spiral form after packing.

TABLE I

DESCRIPTION OF COLUMNS USED FOR GAS–LIQUID PHASE CHROMATOGRAPHY

	Column			
	A	*B*	*C*	*D*
Liquid phase	Gum Rubber Phenyl Methyl GE-SE-52 15%	Versamide 900 15%	Carbowax 750 10%	Reoplex 400 10%
Solid support	Gas Pack WAB	Gas Pack WAB	Gas Pack F	Gas Pack WAB
Mesh size	60–80	60–80	60–80	60–80
Length of column (m)	1.50	1.50	1.50	1.50
Theoretical plates	1000	1100	1000	800
Flow rate (ml He/min)	100	100	100	50–80
Inlet pressure (p.s.i.)	35	35	35	35
Column temperature (°C)	140–200	140–200	140–180	140

The numbers of theoretical plates were determined from chromatograms of different substances, and at different temperatures; the divergence was of about 100 plates. The most consistent results were obtained for the internal standards and for alkylpyridines with saturated side chains. The largest discrepancies were noticed between the straight- and branched-chain alkenylpyridines.

All measurements were made at the highest sensitivities, and special care was taken to avoid overloading the columns. The relative retentions given in Table II are presented in the increasing order on non-polar Silicone Gum column A. They are the averages of a large number of measurements, and the number of significant figures indicate the reproducibility of relative retention values.

RESULTS

Each of the liquid phases tested was able to separate some of the isomers of alkenylpyridines, however, most suitable columns for the analytical and preparative separation of alkenylpyridines were those containing Silicone Gum GE-SE-52, Reoplex 400, Versamide 900, and Carbowax 750 (Table I). The latter permitted also the determination of water in alkylpyridines. For preparative purposes Apiezon L gives satisfactory results, however, for quantitative analysis it cannot be used as alkenylpyridines appear as tailed peaks.

It is well known[18] that the same set of compounds can appear on different columns at different sequences, and this was also confirmed in the present study. Table II contains relative retentions of various substituted 2- and 4-pyridines. These relative retentions were independent of such factors as flow rate, column length, or liquid phase concentration. *n*-Butylcyclohexane and 1,2-diphenylbutane were used as internal standards[19,20] for a quantitative determination of pyridines, obtained from the alkenylation reactions. At least one of these two hydrocarbons did not overlap with the peaks of compounds analyzed. For the quantitative determinations it was imperative to determine the relative responses of the thermal conductivity cells for the substances and the internal standards[19,20]. In the case of γ-picoline *vs.* *n*-butylcyclohexane the ratio was 1.72. The relative retention of the internal standards given in Table II allows calculating the relative retention times of alkenylpyridines from one standard to another.

DISCUSSION

The relative retentions of the various alkyl- and alkenylpyridines (Table II) permit drawing the following conclusions.

In all observed cases the relative retentions of 4-alkylpyridines are higher than those of the corresponding two isomers. On Silicone Gum, column A, they are about 50% higher. On Versamide 900, Reoplex 400, and Carbowax 750, columns B, C, and D, respectively, retentions of two isomers are lower and of four isomers are higher than on column A and in consequence on these columns relative retentions of four isomers are up to two times higher than those of two isomers.

The retention depends on the number of carbon atoms in the side chain, and on the branching of the chain. If the number of the carbon atoms is the same, the more branched the chain is the lower the retention. It seems that for the straight-chain homologues, as well as for homologues with one methyl substituent in the straight chain at the same position with respect to the pyridine ring, there is a linear correlation between retention and the number of the carbon atoms in the chain. The position of the methyl substituent in the chain has also a bearing on the relative retention.

The retention of the alkenylpyridines with identical carbon skeleton depends on the position of the double bond. Retentions of alkenylpyridines containing a double bond in γ position with respect to the pyridine ring are lower than those containing a double bond in the δ position. Configuration is also important and it is a predictable factor. Retentions of *trans* isomers are lower than those of the corresponding *cis* isomers. If alkenylpyridine branched at the benzylic carbon atom contains two double bonds in identical positions with regard to the pyridine ring, the retentions increase in the following order: *trans-trans* < *trans-cis* < *cis-cis*. The largest difference and thus the best separation is achieved on Versamide 900, column B. Similar results were obtained on Reoplex 400 and Carbowax 750, columns C and D. On Silicone Gum, column A, *cis* and *trans* isomers show much closer retentions and thus are often inseparable. Relative retentions of alkylpyridines on Carbowax 750 are close to those on Versamide 900 column, but alkenylpyridines are more retarded on Carbowax and their relative retentions are up to 10% higher.

The retentions of alkylpyridines with saturated side chain on non-polar column A

TABLE II

RELATIVE RETENTIONS OF 2- AND 4-ALKYL- AND ALKENYLPYRIDINES OVER VARIOUS CHROMATOGRAPHIC COLUMNS AND AT VARIOUS TEMPERATURES

No.	*Compound*	*Formula*	*Source*	*A*	
				140°	*160°*
1	Pyridine	C_5H_5N		0.19	0.22
2	α-Picoline	C_6H_7N		0.28	0.34
3	γ-Picoline	C_6H_7N			0.38
4	β-Picoline	C_6H_7N		0.40	0.45
5	2-Ethylpyridine	C_7H_9N		0.49	0.53
6	2-Isopropylpyridine	$C_8H_{11}N$		0.64	0.67
7	4-Ethylpyridine	C_7H_9N		0.71	0.74
8	2-*n*-Propylpyridine	$C_8H_{11}N$	1	0.80	0.83
9	4-Isopropylpyridine	$C_8H_{11}N$		0.96	0.99
10	2-(2-Pyridyl)butane	$C_9H_{13}N$	1	0.99	1.02
11	*n*-Butylcyclohexane	$C_{10}H_{20}$		1.000	1.000
12	4-*n*-Propylpyridine	$C_8H_{11}N$	1	1.14	1.19
13	2-Methyl-2-(2-pyridyl)butane	$C_{10}H_{15}N$	2	1.45	1.39
14	2-Methyl-3-(2-pyridyl)butane	$C_{10}H_{15}N$	2	1.50	1.44
15	3-(2-Pyridyl)pentane	$C_{10}H_{15}N$	1	1.54	1.45
16	1-(4-Pyridyl)-2-methylpropane	$C_9H_{13}N$	2	1.58	1.55
17	2-Methyl-3-(2-pyridyl)pentane	$C_{11}H_{17}N$	2	2.16	2.03
18	2-Methyl-2-(4-pyridyl)butane	$C_{10}H_{15}N$	2	2.47	2.29
19	3-(4-Pyridyl)pentane	$C_{10}H_{15}N$	2	2.50	2.40
20	2-Methyl-2-(4-pyridyl)butane	$C_{10}H_{15}N$	2	2.62	2.45
21	*trans*-5-(4-Pyridyl)-2-pentene	$C_{10}H_{13}N$	4	3.33	3.02
22	1-(4-Pyridyl)pentane	$C_{10}H_{15}N$	4	3.37	3.12
23	Quinoline	C_9H_7N		3.39	3.12
24	*cis*-5-(4-Pyridyl)-2-pentene	$C_{10}H_{13}N$	4	3.51	3.15
25	2-Methyl-3-(4-pyridyl)pentane	$C_{11}H_{17}N$	2	3.54	3.22
26	2,3-Dimethyl-3-(2-pyridyl)pentane	$C_{12}H_{19}N$		3.70	3.25
27	4-Methyl-5-(4-pyridyl)-2-pentene	$C_{11}H_{15}N$	8	4.00	3.48
28	1-(4-Pyridyl)-2-methylpentane	$C_{11}H_{17}N$	8	4.38	3.86
29	2-Methyl-5-(4-pyridyl)pentane	$C_{11}H_{17}N$	4	4.67	4.01
30	1-(4-Pyridyl)-3-methylpentane	$C_{11}H_{17}N$	4	5.07	4.33
31	2-Methyl-5-(4-pyridyl)-2-pentene	$C_{11}H_{15}N$	8	5.23	4.38
32	*trans*-1-(4-Pyridyl)-3-hexene	$C_{11}H_{15}N$	8	5.41	4.70
33	3-Methyl-5-(4-pyridyl)-2-pentene	$C_{11}H_{15}N$	8	5.50	4.62
34	1-(4-Pyridyl)hexane	$C_{11}H_{17}N$	8	5.68	4.82
35	*trans*-4-Methyl-5-(4-pyridyl)-2-hexene	$C_{12}H_{17}N$	8	5.89	5.07
36	*cis*-4-Methyl-5-(4-pyridyl)-2-hexene	$C_{12}H_{17}N$	8	5.89	5.07
37	*trans*-6-(4-Pyridyl)-2-hexene	$C_{11}H_{15}N$	8	5.92	5.04
38	*cis*-6-(4-Pyridyl)-2-hexene	$C_{11}H_{15}N$	8	5.94	5.05
39	*trans*-5-(4-Pyridyl)-2-heptene	$C_{12}H_{17}N$	4	5.97	5.59
40	3-(4-Pyridyl)heptane	$C_{12}H_{19}N$	4	6.27	5.41
41	2-(4-Pyridyl)-3-methylhexane	$C_{12}H_{19}N$	8	6.57	5.71
42	*trans*-6-(4-Pyridyl)-3-heptene	$C_{12}H_{17}N$	8	6.65	5.72
43	*cis*-5-(4-Pyridyl)-2-heptene	$C_{12}H_{17}N$	4	6.52	6.24
44	*trans*-6-(4-Pyridyl)-2-heptene	$C_{12}H_{17}N$	8	7.31	6.31
45	*trans, trans*-5-(4-Pyridyl)nona-2,7-diene	$C_{14}H_{19}N$	4	—	—
46	5-(4-Pyridyl)nonane	$C_{14}H_{23}N$	4	—	8.28
47	*trans,cis*-5-(4-Pyridyl)nona-2,7-diene	$C_{14}H_{19}N$	4	—	—
48	*cis,cis*-5-(4-Pyridyl)nona-2,7-diene	$C_{14}H_{19}N$	4	—	—
49	1,2-Diphenylbutane	$C_{16}H_{18}$		20.58	16.4
50	2,8-Dimethyl-5-(4-pyridyl)nonane	$C_{16}H_{27}N$	4	—	—
51	4,6-Dimethyl-5-(4-pyridyl)nonane	$C_{16}H_{27}N$	8	—	—
52	4-Methyl-5-(4-pyridyl)decane	$C_{16}H_{27}N$	8	—	—
53	2,8-Dimethyl-5-(4-pyridyl)nona-2,7-diene	$C_{16}H_{33}N$	8	—	—
54	6-(4-Pyridyl)undecane	$C_{16}H_{27}N$	8	—	—
55	5-(4-Pyridyl)-5-butylnonane	$C_{18}H_{31}N$	4	—	—

		B				C	D		
80°	200°	140°	160°	180°	200°	140°	140°	160°	180°
—	—	0.06	0.07	0.11	—	0.10	0.09	0.12	—
—	—	0.07	0.098	0.11	—	0.12	0.10	0.12	—
—	—	0.12	0.15	0.18	0.18	0.17	0.17	0.19	—
—	—	0.12	0.14	0.17	—	0.18	0.16	0.19	—
—	—	0.11	0.14	0.16	—	0.16	0.15	0.16	—
—	—	0.12	0.15	0.19	—	0.16	0.16	0.17	—
—	—	0.20	0.24	0.28	—	0.27	0.28	0.30	—
—	—	0.17	0.20	0.22	—	0.23	0.10	0.26	—
—	—	0.28	0.32	0.35	—	0.34	0.14	0.39	—
—	—	0.19	0.22	0.25	—	0.24	0.10	0.26	—
.709	0.092	0.11	0.133	0.155	0.166	0.072	0.053	0.067	0.073
—	—	0.34	0.38	0.41	—	0.41	0.17	0.45	—
—	—	0.25	0.27	0.35	—	0.30	0.12	0.29	—
—	—	0.28	0.31	0.33	—	0.33	0.13	0.33	—
—	—	0.27	0.30	0.32	—	0.33	0.13	0.33	—
—	—	0.43	0.47	0.50	—	0.47	0.20	0.49	—
.15	0.17	0.35	0.38	0.42	0.43	1.06	0.16	0.39	0.40
.17	0.19	0.67	0.70	0.75	0.96	0.69	0.30	0.73	0.46
.18	0.20	0.64	0.68	0.73	0.95	0.68	0.29	0.71	0.73
.19	0.21	0.74	0.76	0.78	0.80	0.76	0.32	0.78	0.84
.22	0.24	1.06	1.06	1.04	1.04	1.24	1.23	1.20	1.20
.22	0.25	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
.24	0.26	1.63	—	1.64	1.67	2.32	2.47	2.36	2.30
.23	0.24	1.13	1.12	1.11	1.10	1.33	1.34	1.30	1.30
.24	0.26	0.91	0.93	0.95	0.95	0.85	0.38	0.90	0.93
.25	0.28	0.64	0.64	0.69	0.71	0.67	0.26	0.64	0.68
.26	0.28	1.09	1.08	1.07	1.06	1.24	1.23	1.22	1.20
.28	0.30	1.22	1.19	1.19	1.13	1.15	1.14	1.14	1.14
.30	0.31	1.34	1.27	1.23	1.21	1.26	1.27	1.24	1.22
.31	0.34	1.46	1.40	1.35	1.30	1.37	1.36	1.33	1.32
.32	0.35	1.55	1.51	1.47	1.42	1.74	1.73	1.60	1.59
.33	0.35	1.61	1.54	1.46	1.41	1.76	1.68	1.60	1.56
.34	0.35	1.74	1.69	1.63	1.58	1.90	1.91	1.77	1.73
.35	0.37	1.70	1.62	1.53	1.47	1.60	1.60	1.48	1.46
.35	0.38	1.53	1.45	1.40	1.35	1.55	1.47	1.41	1.40
.35	0.38	1.64	1.54	1.51	1.46	1.67	1.64	1.56	1.56
.35	0.38	1.90	1.79	1.68	1.59	2.03	1.96	1.84	1.78
.35	0.38	1.98	1.86	1.76	1.69	2.10	2.09	1.95	1.86
.37	0.40	1.71	1.60	1.51	1.42	1.76	1.69	1.58	1.52
.38	0.40	1.59	1.48	1.41	1.36	1.44	1.41	1.33	1.32
.39	0.41	1.75	1.66	1.55	1.50	1.55	1.55	1.49	1.46
.39	0.41	1.88	1.74	1.63	1.56	1.83	1.39	1.65	1.62
.40	0.42	1.98	1.84	1.73	1.66	1.99	1.92	1.78	1.76
.42	0.49	2.16	2.00	1.17	1.76	2.22	2.17	2.01	1.93
.73	0.73	—	—	3.02	2.71	—	—	—	3.10
.77	0.76	—	—	2.74	2.39	—	—	—	2.21
.81	0.80	—	—	3.41	3.06	—	—	—	3.59
.85	0.85	—	—	3.85	3.45	—	—	—	4.06
.000	1.000	4.586	3.98	3.65	3.34	—	5.15	4.59	4.03
.14	1.07	—	—	3.55	3.04	—	—	—	2.72
.22	1.22	—	—	4.21	3.74	—	—	—	3.19
.36	1.34	—	—	4.66	4.08	—	—	—	3.44
.48	1.38	—	—	5.24	4.46	—	—	—	5.23
.62	1.52	—	—	5.71	4.73	—	—	—	4.13
–	2.24	—	—	—	6.61	—	—	—	—

are between those of the corresponding *cis* and *trans* isomers containing a double bond in γ position with respect to the pyridine ring. On the polar columns B, C, and D, retentions of alkylpyridines with saturated side chains are lower than of the corresponding 4-*cis* and *trans* isomers.

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