GAS CHROMATOGRAPHY AND STRUCTURAL CORRELATION OF SUBSTITUTED AZIRIDINES*

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Ethylenimine and its derivatives, the substituted aziridines, are an important class of compounds in industrial and biomedical areas. N-Substituted[1,2], N-carbamoyl[3], sulfur[4,5], and phosphorus[6–10] containing aziridines, have been utilized as insect chemosterilants. Aziridines have also been studied in neoplasms[11–14], as monoamine oxidase inhibitors[15], ion-exchange copolymers[16]; and wear and water proofing[17,18], textile[19–22] and paper improving agents[23,24].

Analysis of aziridines has been effected by colorimetry with γ-(4-nitrobenzoyl)-pyridine[25] and 1,2-naphthoquinone-4-sulfonate[26] and by direct[27] and potentiometric titration[28]. Gas chromatographic analysis of aziridines, however, has been limited to the separation of a *cis* and *trans* alkyl aziridine[29].

This study describes the elution behavior of N-aryl- and N-alkyl-carbamoyl-aziridines on five liquid phases and relates the chromatographic data obtained for the aryl derivatives to the separation of solute moiety–solvent interaction *via* consideration of linear aryl moiety values as interaction products of a solute moiety value and a partitioning phase value.

EXPERIMENTAL

The N-carbamoylaziridine derivatives were synthesized by reaction of ethylenimine with a selection of aryl and alkyl isocyanates in benzene. Ethylenimine was obtained from Chemirad, Inc., East Brunswick, N.J. (U.S.A.). The isocyanates were obtained from various commercial sources.

Gas chromatographic analysis was carried out on 6 ft. by 0.25 in. O.D. glass coiled columns containing alternatively, 3 % Carbowax 20M (polyglycol), 4 % DC QF-1 (trifluoropropylmethyl silicone fluid), 15 % GE Versilube F-50 (chlorophenylmethyl silicone fluid), and 15 % GE XE-60 (cyanoethyl methyl/dimethyl silicone gum), housed in a modified (kit from Applied Science Labs., State College, Pa., U.S.A.) F & M Model 1609 flame ionization instrument such that the samples were injected on-column with the effluent passing directly to the detector. Column temperature was set by an F & M Model 240 power-proportioning controller and the carrier flow was maintained through a Brooks ELF Model 8943 constant downstream flow controller. Analysis on 12 % GE SE-30 (methyl silicone gum) was performed on a 5.5 ft. by 0.25

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in. O.D. copper coiled column in an F & M Model 720 oven containing a hot-wire detector. The specific conditions of analysis for all chromatographic columns are summarized in Table I.

Physical constants of the synthesized aziridines and the respective isocyanates together with literature values where available are given in Table II. With the exception of several of the alkyl derivatives and N-β-phenylethyl-carbamoylaziridine, the synthesized aziridines were all solids. The melting points were obtained on a Fisher-Johns Melting Point Apparatus. Injected samples were of 0.1 to 0.2 μl, generally in acetone solution.

TABLE I

EXPERIMENTAL CONDITIONS

	Columns				
	(1) *QF-1*	(2) *Versilube F-50*	(3) *Carbowax 20M*	(4) *XE-60*	(5) *SE-30*
Column					
% Coating	4 %	15 %	3 %	15 %	12 %
Support	Chromosorb W 80–100 mesh (HMDS)	Chromosorb W 60–80 mesh (HMDS)	Chromosorb G 60–80 mesh (AW-DMCS)	Chromosorb W 60–80 mesh (HMDS)	Chromosorb W 60–80 mesh (HMDS)
Dimensions	6 ft. × 1/4 in. (glass)	6 ft. × 1/4 in. (glass)	6 ft. × 1/4 in. (glass)	6 ft. × 1/4 in. (glass)	5.5 ft. × 1/4 in. (copper)
Conditions					
Column temperature	110° 150°	170° 210°	140° 200°	165°	180°
Injection port	255°	255°	255°	255°	245°
Detector temperature	200°	200°	200°	200°	250°
N_2, ml/min	33 37	45 46	69 119	61	33[a]
Detector	F.I.	F.I.	F.I.	F.I.	T.C.

[a] He, ml/min.

RESULTS AND DISCUSSION

Retention data for the aziridine derivatives, relative to N-*n*-propyl-carbamoylaziridine, on the QF-1 and Versilube F-50 liquid phases are given in Table III. Overall, retention and resolution were generally greater on the latter than on the former phase. Elution distinctions for isomeric aryl families may be discerned, as may the categoric retention order of $NO_2 > CN > CH_3O$, $Br > Cl > CH_3 > F$.

The chromatographic results of the aziridines measured on four of the partitioning phases employed (chromatography on XE-60 to be discussed below), expressed relative to N-phenyl-carbamoylaziridine and as KOVÁTS hydrocarbon retention indices, are shown in Table IV. The isocyanate precursors to the respective aziridine derivatives were included in the analyses performed on QF-1. It was observed with interest and concern that the retention of the aryl derivatives was fairly close to that of their respective isocyanates in a number of instances. The slight differences obtained, however, were consistently reproducible—the isocyanate (with the exception of the naphthyl and *p*-cyanophenyl derivatives) always eluting slightly ahead of the corresponding aziridine. On the polar Carbowax 20M liquid phase, N-phenyl-carbamoylaziridine had an elution time of 1.80 min, while phenyl isocyanate eluted in

TABLE II

PHYSICAL CONSTANTS (M.P. AND B.P.) OF ISOCYANATES AND N-CARBAMOYLAZIRIDINES

	$R-N=C=O$	$R-N(H)-C(=O)-N\langle CH_2-CH_2 \rangle$	
R	*Isocyanate (°C) (mm)*	*Aziridine (°C) (mm)*	
		Found	*Literature*
Methyl	37–39[a]	35–37 (0.4)[a]	—
Ethyl	59–61[a]	51–53 (0.4)[a]	—
Propyl	87–88[a]	69–71 (0.4)[a]	—
Isopropyl	73–75[a]	50–52	—
Butyl	110–114[a]	84–86 (0.4)[a]	85–87 (0.4)[a,b]
Phenyl	54–55 (13)[a]	79–81	82–83[d]
Cyclohexyl	166–168[a]	78–80	81–82[c]
o-Tolyl	184–186[a]	73.5–75	75–76[b]
m-Tolyl	75–76 (12)[a]	69–70.5	70.5–71.5[b]
p-Tolyl	70–72 (10)[a]	97–99	98.5–99.5[b]
p-Fluorophenyl	71–73 (29)[a]	73–75	—
o-Methoxyphenyl	93–94 (7)[a]	63–64.5	64–65[b]
p-Methoxyphenyl	(−11)–(−9)[a]	114–116	114–115.5[b]
o-Chlorophenyl	(−5)–(−3)[a]	51–53	52–53.5[b]
m-Chlorophenyl	76–78 (10)[a]	92–94	92.5–94[b]
p-Chlorophenyl	29.5–30.5	133–135	132–133.5[b]
m-Trifluormethylphenyl	54 (11)[a]	73–74	—
p-Bromophenyl	41–42.5	141–143	138.8–139.5[d]
β-Phenethyl	98–100 (10)[a]	127–129	—
α-Naphthyl	3–5	107–108	108–109[b]
p-Cyanophenyl	102–104	131–133	—
o-Nitrophenyl	38–39	227–230	—
m-Nitrophenyl	52–53.5	135–137	—
p-Nitrophenyl	57–59	171–172	164 dec[b]

[a] Boiling points.
[b] A. B. BOŘKOVEC AND C. W. WOODS, *J. Med. Pharm. Chem.*, 8 (1965) 545.
[c] E. BESTIAN, J. HEYNA, A. BAUER, G. EHLERS, B. HIRSEKORN, T. JACOBS, W. NOLL, W. WEIBEZAHN AND F. ROMER, *Ann.*, 566 (1950) 210.
[d] B. C. FISCHBACK AND G. H. HARRIS, *U.S. Pat.*, 2,775,587, Dec. 25, 1956; *C.A.*, 51 (1957) 9700.

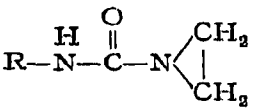
0.7 min (column temperature, 140°). A considerable retention difference was observed for the N-alkyl-carbamoylaziridines *vs.* their respective isocyanates, illustrating the contribution to retention introduced by condensation of the ethylenimine ring with the low boiling alkyl isocyanates. The retention relative to N-phenyl-carbamoylaziridine was less for hydrocarbon structures (*e.g.* the tolyl derivatives) on Carbowax 20M than on the silicone phases. For the same reason (*i.e.* diminished extent of interaction of Carbowax 20M with non-polar hydrocarbon solutes*), the highest index values were obtained on the polar Carbowax 20M phase.

Anomalous results were obtained on the XE-60 stationary phase, where it was

* Index values were determined using a C-10 to C-18 *n*-hydrocarbon mixture obtained from Applied Science Laboratories, State College, Pa. (U.S.A.).

TABLE III

N-CARBAMOYLAZIRIDINES RELATIVE TO N-*n*-PROPYLCARBAMOYLAZIRIDINE



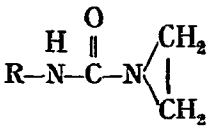
Compound No.	*R*	*QF-1*[a]	*Versilube F-50*[b]
1	ϕ	0.24	0.50
2	*p*-Fϕ	0.30	0.55
3	Cyclohexyl	0.36	—
4	*m*-$CF_3\phi$	0.38	0.59
5	*o*-Tolyl	0.41	0.73
6	*m*-Tolyl	0.43	0.81
7	*p*-Tolyl	0.44	0.92
8	Methyl	0.47	0.61
9	Ethyl	0.62	0.69
10	*o*-Clϕ	0.66	0.94
11	*m*-Clϕ	0.64	1.14
12	*p*-Clϕ	0.69	1.28
13	β-ϕC_2H_4	0.75	–
14	Isopropyl	0.90	0.74
15	*n*-Propyl[c]	1.00	1.00
16	*p*-Brϕ	1.14	1.74
17	*o*-Methoxyϕ	1.19	1.53
18	*p*-Methoxyϕ	1.32	1.62
19	*n*-Butyl	1.43	1.71
20	α-Naphthyl	3.05	4.53
21	*p*-CNϕ	3.33	3.31
22	*o*-$NO_2\phi$	4.23	—
23	*m*-$NO_2\phi$	4.66	—
24	*p*-$NO_2\phi$	4.72	—

[a] Column temperature 110° for compounds 1–19; 150° for compounds 20–24.
[b] Column temperature 210° for compounds 20 and 21; 170° for all other compounds.
[c] Representative adjusted retention time (min) for the N-*n*-propyl carbamoylaziridine standard: 6.82 on QF-1 (110°), 2.00 on QF-1 (150°), 3.30 on Versilube F-50 (170°), 1.25 on Versilube F-50 (210°).

observed that chromatography resulted in two peaks on the recorder chart for each sample analyzed, including the N-phenyl-carbamoylaziridine standard. Neither of the peaks were commonly present in all samples analyzed, belying lysis to a common degradation product (*e.g.* a fragment structure containing the ethylenimine ring). The first peak was found to coincide precisely with the respective parent isocyanate while the second peak matched the respective aniline derivative. The formation of aniline derivatives was further substantiated by the positive Hinsberg test obtained by bubbling the effluent gas from the chromatograph directly into a small amount of test reagent in a small tube. This latter step was carried out on an F & M Model 500 chromatograph equipped with a Model 720 dual column oven and a hot-wire detector. A copper column (8 ft. by 0.125 in. O.D.) was used with the same liquid phase load

TABLE IV

N-CARBAMOYLAZIRIDINES RELATIVE TO N-PHENYLCARBAMOYLAZIRIDINE AND KOVÁTS INDICES



Compound No.	*R*	*SE-30*		*Versilube F-50*[a]		*QF-1*[b]			*Carbowax 20M*[c]	
		Aziridine/ N-Phenyl	*Index*	*Aziridine/ N-Phenyl*	*Index*	*Aziridine/ N-Phenyl*	*Isocyanate/ N-Phenyl*	*Aziridine Index*	*Aziridine/ N-Phenyl*	*Index*
1	ϕ[d]	1.00	1007	1.00	976	1.00	1.00	1187	1.00	1638
2	*p*-Fϕ	1.06	1020	1.10	997	1.24	1.14	1228	1.78	1759
3	Cyclohexyl	—	—	—	—	1.48	1.48	1261	0.21	568
4	*m*-$CF_3\phi$	1.13	1035	1.18	1010	1.58	1.29	1273	2.74	1850
5	*o*-Tolyl	1.46	1097	1.46	1054	1.70	1.69	1287	0.56	1516
6	*m*-Tolyl	1.50	1103	1.61	1075	1.77	1.72	1294	1.00	1638
7	*p*-Tolyl	1.60	1118	1.84	1103	1.83	1.79	1301	1.03	1645
8	Methyl	—	—	1.21	1016	1.96	—0.03	1314	—	—
9	Ethyl	—	—	1.38	1043	2.58	0.03	1365	—	—
10	*o*-Clϕ	1.82	1148	1.87	1106	2.74	2.62	1377	3.53	1902
11	*m*-Clϕ	2.32	1204	2.28	1148	2.65	2.45	1371	[e]	[e]
12	*p*-Clϕ	2.37	1208	2.56	1172	2.86	2.72	1385	[e]	[e]
13	β-oC_2H_4	—	—	—	—	3.09	3.03	1399	—	—
14	Isopropyl	—	—	1.47	1056	3.72	0.03	1436	—	—
15	*n*-Propyl	—	—	2.00	1121	4.13	0.11	1456	—	—
16	*p*-Brϕ	4.52	1348	3.48	1236	4.71	4.71	1482	13.4	2182
17	*o*-Methoxyϕ	2.53	1223	3.06	1208	4.93	4.76	1491	2.59	1838
18	*p*-Methoxyϕ	2.76	1242	3.24	1221	5.45	5.24	1511	[f]	[f]
19	*n*-Butyl	—	—	3.41	1232	5.90	0.29	1526	[g]	[g]
20	α-Naphthyl	—	—	9.06	1523	12.6	12.7	1807	—	—
21	*p*-CNϕ	6.22	1420	6.62	1439	12.1	13.7	1830	[f]	[f]
22	*o*-$NO_2\phi$	—	—	—	—	17.5	15.9	1887	—	—
23	*m*-$NO_2\phi$	—	—	—	—	19.3	16.6	1912	—	—
24	*p*-$NO_2\phi$	—	—	—	—	19.5	18.1	1915	—	—

[a] Column temperature 210° for compounds 20 and 21; 170° for all other compounds.

[b] Column temperature 110° for compounds 1–19; 150° for compounds 20–24.

[c] Column temperature 200° for compounds 16 and 18; 140° for all other compounds.

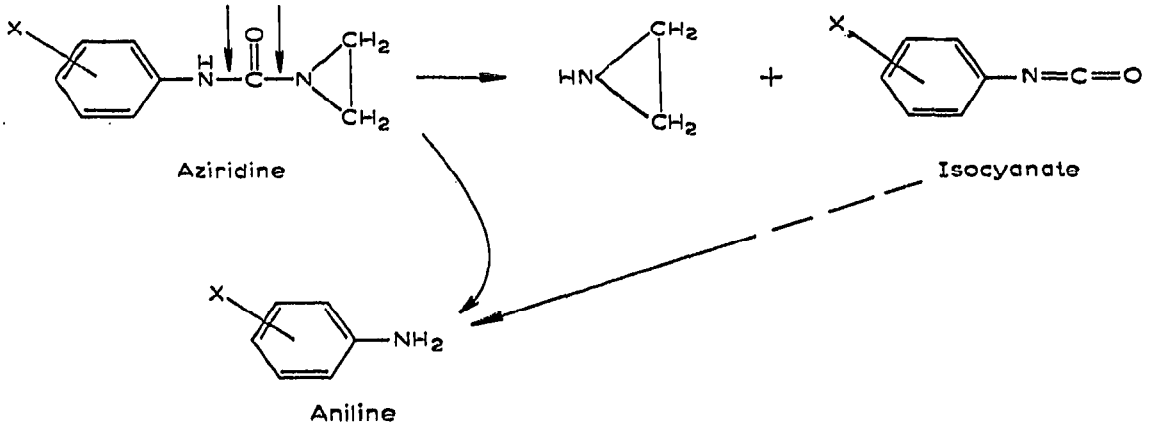
[d] Representative adjusted retention time (min) for N-phenyl-carbamoylaziridine standard: 1.30 on SE-30, 1.70 on Versilube F-50 (170°), 0.65 on Versilube F-50 (210°), 1.65 on QF-1 (110°), 0.50 on QF-1 (150°), 1.80 on Carbowax 20M (140°), 0.28 on Carbowax 20M (200°).

[e] Decomposed.

[f] Not detected.

[g] Eluted in solvent peak.

(15% XE-60 on 60–80 mesh HMDS-Chromosorb W). The chromatographic observations on XE-60 may be illustrated as follows:

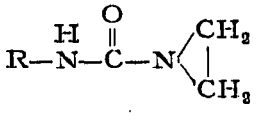


Owing to the difficulty involved in accounting for the conversion of isocyanate to aniline, it is felt that the aniline products may result directly during initial cleavage of the aziridines.

As may be seen in Table V, the N-alkyl derivatives did not degrade. Degradation of the isomeric tolyl derivatives interestingly gave varying aniline/isocyanate peak area ratios (Table VI). The *ortho* isomer produced considerably less aniline product. The

TABLE V

CHROMATOGRAPHY ON 15% XE-60



Compound No.	*R*	*Isocyanate index*[b]	*Aniline index*[b]
1	ϕ	1340	1506
2	*p*-Fϕ	1334	1563
5	*o*-$CH_3\phi$	1400	1573
6	*m*-$CH_3\phi$	1407	1605
7	*p*-$CH_3\phi$	1407	1569
11	*o*-Clϕ	—	1666
17	*o*-$CH_3O\phi$	1643	1698
18	*p*-$CH_3O\phi$	1659	1808
10	*m*-Clϕ	—	1823
12	*p*-Clϕ	—	1829
16	*p*-Brϕ	—	1947
21	*p*-CNϕ[a]	—	—
		Index	
N-Butyl-carbamoylaziridine		1796	
Butyl isocyanate		965	
Butylamine		in solvent front	

[a] Not detected.

[b] Representative adjusted retention time (min) for the standard hydrocarbon mixture: C-10 (0.25), C-12 (0.81), C-14 (1.85), C-16 (4.20), C-18 (9.45).

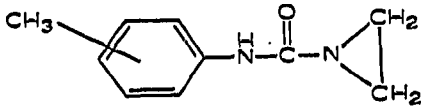
reasons for solute lysis on XE-60 and not on other substrates is not known although there is apparently an early catalytic interaction of the XE-60 solvent phase with the injected solute molecules.

The relative influence of various *para* substituents on the elution of N-aryl-carbamoylaziridines is presented in Table VII for each of the stationary phases employed. The phases are roughly arranged in order of increasing index values (see also Table IV), thereby suggesting their relative order of increasing polarity. With the exception of XE-60, on which aziridine degradation effects were noted, a general increase in the relative influence values of Table VII was observed (relative to the non-polar *p*-methyl substituent) with increasing stationary phase polarity. This should be greater with the more polar solutes as a result of the enhanced dipole–dipole interactions with the stationary solvent.

In interpretation of the analytical chromatographic data, one may go further and ascribe values to the individual aryl moieties based upon the numerical loga-

TABLE VI

DEGRADATION OF ISOMERIC N-TOLYL-CARBAMOYLAZIRIDINES ON XE-60

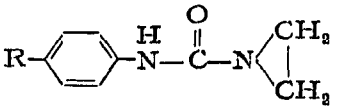


Position	*Area (%)*[a]		*Aniline/isocyanate*
	Isocyanate	*Aniline*	
Ortho	65.3	34.7	0.5
Meta	25.9	74.1	2.9
Para	22.8	77.2	3.6

[a] Based on relative chromatogram peak areas.

TABLE VII

RELATIVE INFLUENCE OF *para* SUBSTITUENTS OF N-ARYL-CARBAMOYLAZIRIDINES ON RETENTION[a]



R	*Mol. wt. of R*	*Relative influence*[a]				
		SE-30	*F-50*	*QF-1*	*XE-60*[b]	*C20-M*
Methyl	15.0	1.00	1.00	1.00	1.00/1.12	1.00
Fluoro	19.0	0.91	0.90	0.94	0.95/1.11	1.07
Cyano	26.0	1.27	1.31	1.41	—	—
Methoxy	31.0	1.11	1.11	1.16	1.18/1.28	—
Chloro	35.4	1.08	1.06	1.06	— /1.30	—
Nitro	50.0	—	—	1.47	—	—
Bromo	79.9	1.21	1.12	1.14	— /1.38	1.33

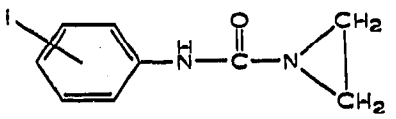
[a] Obtained by ratioing the hydrocarbon index values of the aziridines to the index value obtained for *p*-tolyl-carbamoylaziridine on each liquid phase.

[b] Values given as isocyanate/aniline, relative to *p*-tolyl isocyanate.

rithmic differences of the elution data between the various substituted N-aryl-carbamoylaziridines and N-phenyl-carbamoylaziridine, for each liquid phase. This method had been used earlier for evaluating the relative moiety contributions to the gas chromatographic retention of 3,4-methylenedioxyphenyl derivatives in which the log differences were determined relative to methylenedioxybenzene[30]. The rationale for this type of calculation obviously lies with the well known observation that isothermal gas chromatographic elution is a logarithmic function. The contribution of structural moieties to chromatographic behavior was early recognized by MARTIN[31] prior to the gas chromatographic era. Moiety values resulting from logarithmic calculations with retention data were shown to be additive by KOVÁTS[32,33], KNIGHTS[34,35] and in earlier work by the authors with N-substituted and simple carbamates[36]. Moiety values for the aryl substituents in the N-aryl-carbamoylaziridines are given Table VIII. They infer the relative linear contributions of the aryl substituents toward the chromatographic behavior reported in Tables III and IV, and suggest the relative overall degree of interaction of the solute moiety with the liquid phase.

TABLE VIII

ARYL MOIETY VALUES (M)[a]



i	(*s*) *SE-30*	*F-50*	*QF-1*	*Ca-M*
H	0.000	0.000	0.000	0.000
p-F	0.025	0.041	0.093	0.250
m-CF_3	0.053	0.072	0.199	—
o-CH_3	0.164	0.164	0.230	—0.252
m-CH_3	0.176	0.207	0.248	0.000
p-CH_3	0.204	0.265	0.263	0.013
o-Cl	0.260	0.272	0.438	0.548
m-Cl	0.366	0.358	0.423	—
p-Cl	0.375	0.408	0.456	—
o-CH_3O	0.403	0.486	0.693	0.413
p-CH_3O	0.441	0.510	0.736	—
p-Br	0.665	0.543	0.673	1.127
p-CN	0.794	0.821	1.083	—
o-NO_2	—	—	1.243	—
m-NO_2	—	—	1.290	—

[a] Obtained from: log $R.E._{x+i}$ —log $R.E._x$.

It is possible to delineate these interactions somewhat by a consideration of the moiety values of Table VIII as interaction products of the solute moiety with the non-mobile solvent phase in a manner analogous to the Hammett calculations for substituent values from equilibrium or rate constants in organic reactions[37]. If such dissection were quantitatively descriptive, moiety values could be obtained which, in principle, would be independent of the liquid phase, and a liquid phase selectivity scale might be attainable. Such a simplified approach obviously contains several inherent errors (*e.g.* the aggregation of induction, dispersion and hydrogen bonding

forces into a net interaction value, and the assumption that the differences in the electronic induction effect of the various aryl substituents on the "polarity" of the residual portion of the aziridine molecule and relative to N-phenyl-carbamoyl-aziridine, are negligible). The results of this semi-quantitative/qualitative approach towards a selectivity scale for the liquid phases employed in this study is, nonetheless, somewhat interesting and may be described as follows:

The relatively low polar (methyl silicone polymer) SE-30 phase was arbitrarily designated a relative selectivity of 1.00. Consideration of the Hammett equation proposes a similar equation for gas chromatographic interaction as

$$\log R.E._{x+i} - \log R.E._x = M_i = ps$$

where $R.E.$ = relative elution; M_i = moiety value (additive); p = relative selectivity of liquid phase; s = substituent value; and the M_i values for SE-30 in Table VIII become the s substituent values.

In the expression $M_i = ps$, one has a linear equation possessing a slope of p and an intercept of zero. The greatest point scatter was obtained for Carbowax 20M. The calculated slopes together with their standard deviations are given in Table IX. The observation that this approach suggests a selectivity scale for the liquid phases employed in this study towards the aziridine solutes analyzed is clear when the difference $M_i - M_j = p_A(s_i - s_j)$ for two substituents on column A is algebraically compared to $p_B(s_i - s_j)$ for the same two substituents on column B. If $p_B(s_i - s_j) > p_A(s_i - s_j)$ and $(s_i - s_j)$ approximates a constant, then $p_B > p_A$, which proposes that column B is more selective than column A for the separation of the two aziridines containing substituents i and j, respectively.

TABLE IX

SELECTIVITY SCALE FOR LIQUID PHASES

Phase	*P*	*Standard deviation*
SE-30	1.00	0.00
Versilube F-50	1.18	0.23
QF-1	1.42	0.24
Carbowax 20M	1.60	0.45

The paucity of ample data in the approach discussed above for delineation of solute–solvent interactions is readily conceded. Doubtlessly more reliable and, perhaps, more general selectivity values could be determined if a model block-type experiment could be designed such that varying degrees of polarity in solutes and stationary phases were represented. Delineation of solute–solvent interactions would likewise be improved if one could quantitatively isolate the various attractive forces comprising such interactions.

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SUMMARY

A diverse selection of alkyl and substituted aryl N-carbamoylaziridines were prepared *via* reaction of ethylenimine and various isocyanates. The gas chromatographic behavior of these derivatives was reported on five liquid phases and the data obtained reported relative to N-phenyl-carbamoylaziridine and as KOVÁTS' indices. Degradation to the isocyanate and the aniline derivatives was observed for aryl aziridines on XE-60. The N-alkyl-aziridines were found to chromatograph without thermal rupture. To correlate structural features with the analytical results, structural and positional moiety values were obtained from the log differences of the N-aryl-carbamoylaziridines with N-phenyl-carbamoylaziridine in a manner similar to which the sigma–rho product is obtained in the Hammett equation from equilibrium or rate constants in organic reactions. Separations of *o*, *m* and *p* substituted N-chlorophenyl derivatives were successful.

The influence of functionality in the *para* position of N-aryl derivatives revealed an elution order of $F < CH_3 < Cl < Br, CH_3O < CN$.

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