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CHROMATOGRAPHY OF ORGANOMETALLIC AND ORGANOMETALLOIDAL DERIVATIVES OF AMINO ALCOHOLS

IV. COMPARISON OF RETENTION BEHAVIOUR IN GAS–LIQUID, THIN-LAYER AND HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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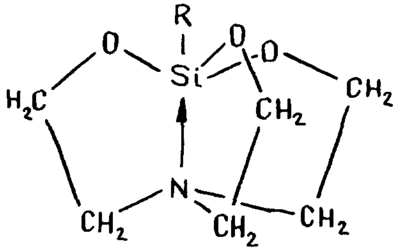
SUMMARY

The applicability of thin-layer and high-performance liquid chromatography for separation of organometalloid derivatives of amino alcohols has been demonstrated. Diastereomers have been separated for several compounds. The relative amounts of the isomers have been shown to depend on the number and nature of the substituents. The way in which the substituents influence retention is similar to that observed earlier in gas–liquid chromatography (GLC). A relationship between the capacity factors on Zorbax CN and the logarithm of the concentration of the mobile phase polar component can be expressed by linear equations. In the reversed-phase mode, retention is linearly correlated with the sum of Rekker's hydrophobic fragmental constants for the substituents. A model is proposed which allows the retention in the reversed-phase mode to be evaluated from GLC retention parameters.

INTRODUCTION

The results of gas–liquid chromatographic (GLC) investigations of organometalloid derivatives of amino alcohols were summarized in our previous publications$^{1-3}$. It has been shown that the existence of a transannular bond between the nitrogen atom and element M and subsequent formation of the so-called atrane



structure promotes retention. Analysis of structure–retention relationships and other physico-chemical data led to the conclusion that enhanced solute–sorbent interaction is mainly due to the specific conformation of compounds with a coordinate N → M bond, which favours interaction between the oxygen atoms and the polar fragments of the stationary phase molecules. It has been shown that retention parameters can serve as an indication of the existence of such a coordinate bond in a given compound under GLC conditions.

Planar and column liquid chromatography are more versatile methods of separation than GLC, which has proved useful only for relatively volatile atranes with moderately polar substituents. Consequently, it is important to what extent the behaviour found in GLC can be extended to atranes in liquid chromatography. The aim of this paper is to compare retention parameters found in liquid chromatography with those observed earlier in GLC.

EXPERIMENTAL

Silufol UV-254 (Kavalier, Czechoslovakia) silica gel plates were used for thin-layer chromatography (TLC). The mobile phases consisted of isopropanol and hexane. Iodine vapour was used for visualization of compounds as light brown spots. A more clear-cut distinction of dark blue spots was achieved by subsequent wetting of the plates with water. The R_M values for the compounds studied were calculated according to the standard expression:

$$R_M = \log\left(\frac{1}{R_F} - 1\right) \tag{1}$$

High-performance liquid chromatographic (HPLC) capacity factors were measured using a Model 8500 Varian and a Model 8800 Dupont liquid chromatograph. Zorbax ODS (250 mm × 4.6 mm) and MicroPak CH-10 (250 mm × 2.1 mm) reversed-phase columns and a Zorbax CN polar bonded phase column were used. The samples were injected with a Model 7125 Rheodyne injector as solutions in the mobile phase. The sample volume was 10–100 μl and the solute concentration was 0.2–1 mg/ml. Mixtures of hexane with isopropanol, dioxane or chloroform were used as mobile phases in the normal-phase mode, acetonitrile–water mixtures in the reversed-phase mode. A spectrophotometer (240 or 254 nm) was used for detection. Capacity factors were calculated as the mean value of three to five measurements according to the usual formula

$$k' = \frac{t_R - t_0}{t_0} \tag{2}$$

where t_R is the retention time of the compounds studied and t_0 is the emergence time of unretained compounds.

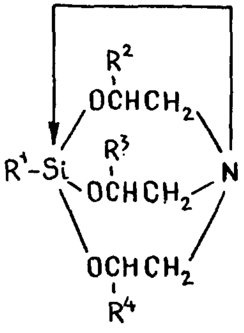
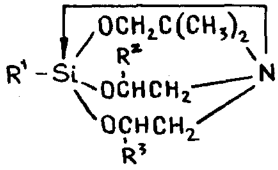
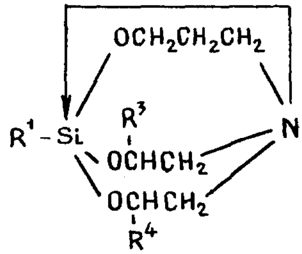
Sodium nitrate was used as the conditionally unretained solute in the reversed-phase mode, and carbon tetrachloride in the normal-phase mode. The reproducibility of k' values was usually no less than $\pm 3\%$ for compounds with $k' > 1$.

RESULTS AND DISCUSSION

Preliminary experiments with 25 atranes and related compounds have shown that under TLC conditions these solutes do not undergo any chemical reactions, and, consequently, the method can be used for their analysis. The R_F values were reproducible within 0.03 R_F units. This enabled us to discuss the relationship between the

TABLE I

R_M VALUES IN ISOPROPANOL–HEXANE (1:1) AS MOBILE PHASE

Compound No.	*General formula*	*Substituents*				R_M
		R^1	R^2	R^3	R^4	
1		H	H	H	H	1.99
2		H	CH_3	CH_3	CH_3	0.50
3		CH_3	H	H	H	0.83
4		CH_3	CH_3	H	H	0.58
5		CH_3	CH_3	CH_3	H	0.48
6		CH_3	CH_3	CH_3	CH_3	0.09
7		CH_3	C_6H_5	H	H	0.69
8		$CH_2=CH$	H	H	H	1.28
9		$CH_2=CH$	C_6H_5	H	H	0.41
10		$CH_2=CH$	C_6H_5	C_6H_5	H	−0.58*
11		C_2H_5O	CH_3	H	H	1.06
12		C_2H_5O	CH_3	CH_3	CH_3	0.43
13		C_6H_5	H	H	H	0.72
14		C_6H_5	CH_3	H	H	0.27
15		C_6H_5	CH_3	CH_3	H	−0.12
16		C_6H_5	CH_3	CH_3	CH_3	−0.66
17		C_6H_5	C_6H_5	H	H	0.09
18		C_6H_5	C_6H_5	C_6H_5	H	−0.10 −1.20
19		C_6H_5O	H	H	H	1.38
20		$C_6H_5CH_2CH_2$	H	H	H	0.63
21		$C_{10}H_7$**	H	H	H	0.50
22		C_6H_5	CH_3	CH_3	–	−0.72*
23		$CH_2=CH$	H	H	–	0.0
24		$CH_2=CH$	CH_3	CH_3	–	0.95 −0.50 −0.87
25		C_6H_5	–	CH_3	CH_3	−0.19

* The spot is asymmetric due to partial separation of the isomers.

** $C_{10}H_7$ is α-naphthyl.

retention and the chemical structure of the solutes. The R_M values are summarized in Table I.

It is generally believed that the polarity of solutes is the main factor responsible for retention on silica gel. On the other hand, the gas chromatographic retention parameter ΔI, which is equal to the difference in retention indices for a given solute on polar and non-polar stationary phases, can be used as a measure of solute polarity exhibited in chromatographic experiments. Hence, it would be natural to expect some degree of correlation between R_M and ΔI. These parameters are compared in Fig. 1.

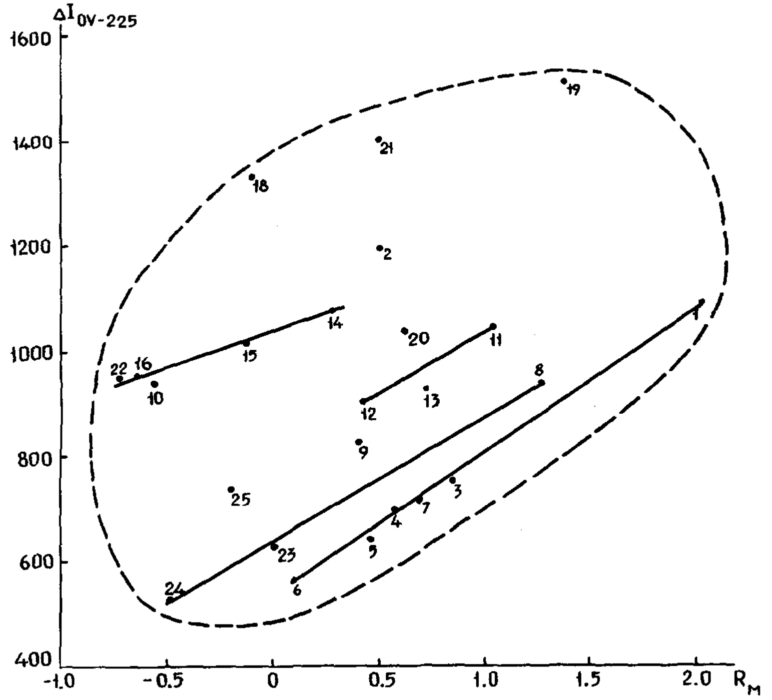


Fig. 1. Relationship between ΔI values in GLC on the polar stationary phase OV-225 and R_M values on Silufol TLC plates. The straight lines connect points corresponding to closely related compounds.

The area occupied by the experimental points shows only a slight increase in R_M values with increasing ΔI values. No correlation between R_M and ΔI is observed when the compounds under study are regarded as members of the same class. This signifies that the above interpretation of chromatographic polarity and its influence on retention is oversimplified. For example, in terms of the chromatographic behaviour, the introduction of an additional methylene group into the solute molecule has an insignificant effect on its polarity, and the ΔI values for such homologues are usually very similar. The situation is more complex in liquid chromatography on silica, where the retention can be highly sensitive to the number of methylene groups present in the solute molecule within one group of solutes, or completely insensitive within other groups.

Nevertheless, if closely related compounds are compared, one can see that the solute structure has similar influences on the TLC and GLC behaviours. For example, consecutive substitution of hydrogen atoms for methyl groups in the atrane ring leads to a decrease in R_M and ΔI values, which are correlated within this group of solutes. Similarly, the introduction of additional methylene groups into the atrane framework results in decreased retention in TLC (compounds 15 and 25, 8 and 23).

Generally, the high efficiency of the TLC plates and an high degree of selectivity of the solvent system used are not enough to resolve diastereomers. The separation and detection of atrane diastereomers as distinct spots has been achieved only in a few cases (Table I, Fig. 2).

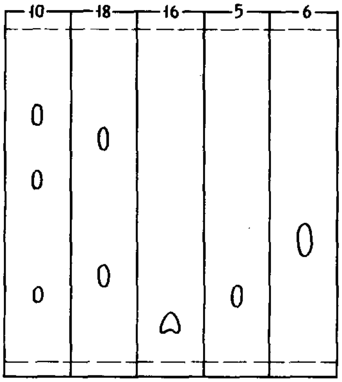


Fig. 2. The behaviour of some diastereomeric atranes in TLC. The numbers correspond to compounds in Table I. Mobile phase: isopropanol–hexane (1:3) (compounds 5, 6, 10, 18) and (1:1) (compound 16).

HPLC retention data on the polar stationary phase Zorbax CN with a mobile phase of hexane–isopropanol (9:1) are given in Table II. There is considerable analogy between the GLC and normal-phase HPLC behaviours.

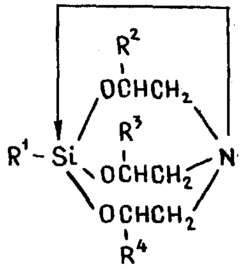
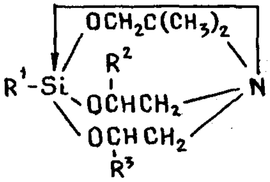
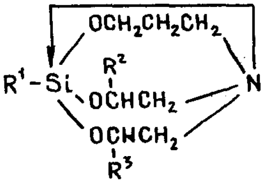
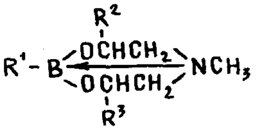
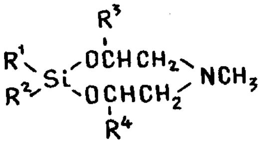
A chromatogram of three compounds having similar functional groups and hydrocarbon moieties is given in Fig. 3. It is seen that the stronger retention of the triethanolamine derivatives compared with the diethanolamine analogue, observed earlier in GLC[3], takes place also in normal-phase HPLC.

A substitution of hydrogen atoms by methyl groups in 1-phenylsilatrane leads to decreased $\delta I_{N \rightarrow Si}$ values in GLC and to a similar decrease of k' in HPLC (Fig. 4). Generally, the log k' values are well correlated with $\delta I_{N \rightarrow Si}$ (Fig. 5) and the correlation is valid for a relatively broad family of solutes including diethanolamine derivatives. An interesting exception is provided by compound 28, $(C_6H_5)_2Si(OCH_2CH_2)_2NCH_3$, which has been shown to possess a transannular N → Si bond and an atrane-like structure in the solid state or in solution at room temperature[4,5]. By contrast, GLC data at 160–250°C showed no evidence of either of them. Obviously, the probability that such a coordinate bond exists is greater at lower temperatures. It is possible then that the observed deviation of compound 28 from the correlation plot is a manifestation of N → Si interaction.

A more detailed study of the relationship between retention and the type and concentration of the polar component of the mobile phase was undertaken for several

TABLE II

CAPACITY FACTORS AND DIASTEREOMER RATIOS OF ALKANOLAMINE DERIVATIVES IN ISOPROPANOL–HEXANE (1:9) AS MOBILE PHASE

Compound No.	*General formula*	*Substituents*				*k'*	*Diastereomer ratio*
		R^1	*R^2*	*R^3*	*R^4*		
10		$CH_2=CH$	C_6H_5	C_6H_5	H	3.04 4.36	1:3.6
13		C_6H_5	H	H	H	7.55	
15		C_6H_5	CH_3	CH_3	H	3.00 3.10 3.27	1:1:2
16		C_6H_5	CH_3	CH_3	CH_3	2.17 2.32	2.8:1
18		C_6H_5	C_6H_5	C_6H_5	H	4.76 5.85	2.6:1
22		C_6H_5	CH_3	CH_3	–	2.06 2.82	1:1.3
26		C_6H_5	CH_3	CH_3	–	0.84 1.30	1:1.8
27		C_6H_5	CH_3	CH_3	–	1.40	
28		C_6H_5	C_6H_5	H	H	2.24	
29		C_6H_5	CH_3	CH_3	H	0.21 0.25	1:1

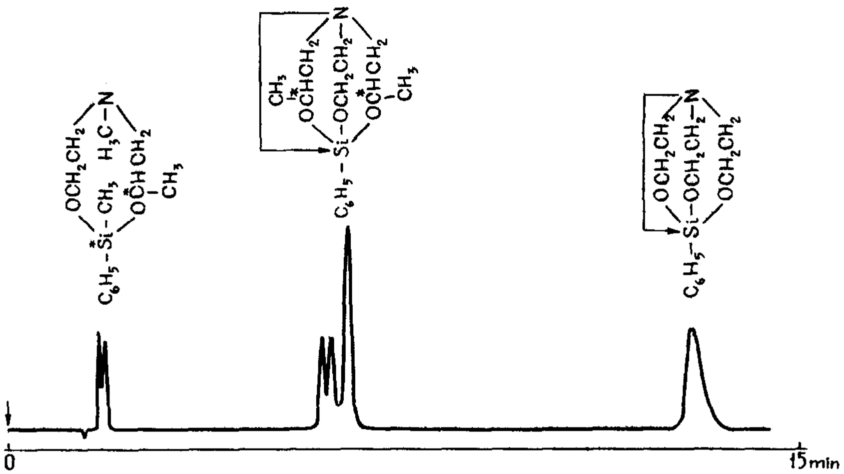


Fig. 3. Separation of di- and triethanolamine derivatives on Zorbax CN.

typical solutes. The results are summarized in Table III. Analysis of these data shows that the linear equation

$$\log k' = a + b \log C \tag{3}$$

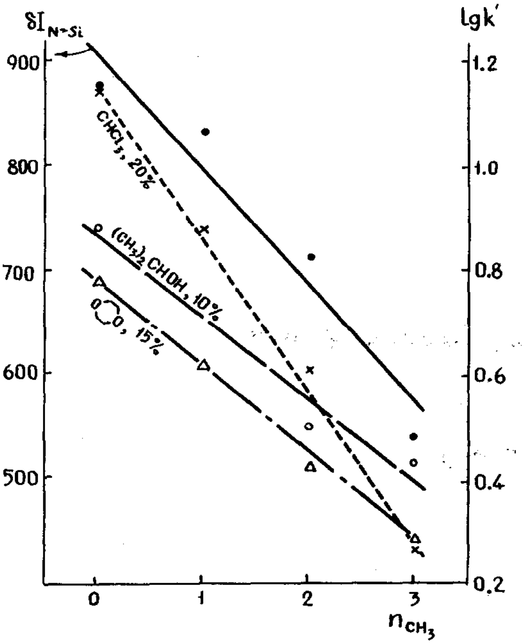


Fig. 4. Influence of the number of methyl substituents in 1-phenylsilatrane in GLC ($\delta I_{N \to Si}$) and in HPLC ($\log k'$) on Zorbax CN. ● = GLC data; × = HPLC, chloroform–hexane (20:80); ○ = HPLC, isopropanol–hexane (10:90); △ = HPLC, dioxane–hexane (15:85).

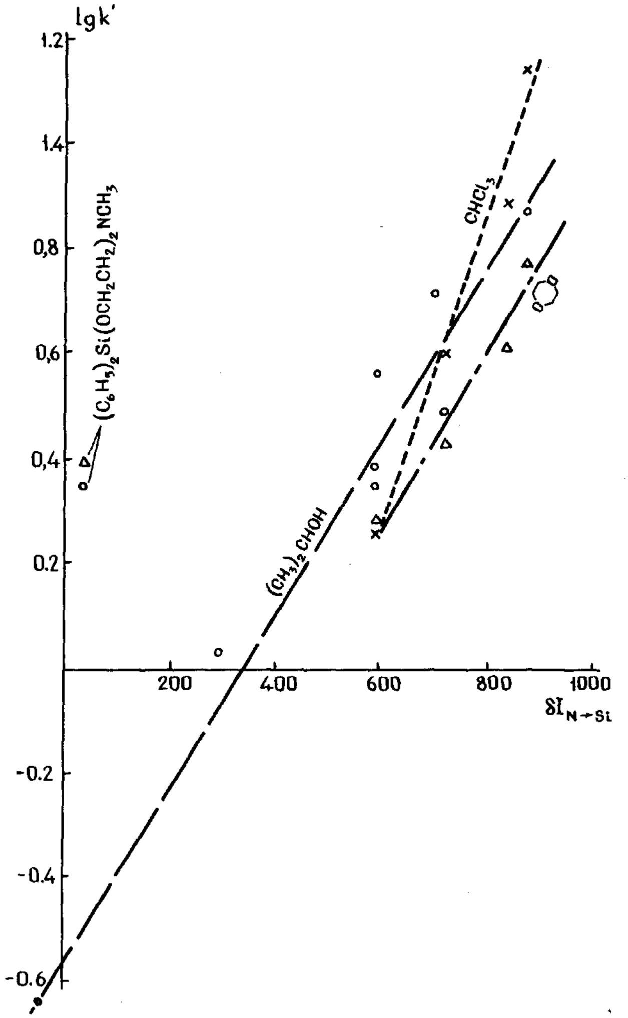


Fig. 5. Relationship between log *k'* on a Zorbax CN column and $\delta I_{N\to Si}$ on OV-225 as stationary phase.

is valid, where *C* is the concentration of the polar component in the mobile phase in % (v/v) and *a*, *b* are coefficients. The parameters of eqn. 3 are given in Table IV. The slope, *b*, does not differ significantly for different compounds, indicating that an approximately equal number of molecules of the polar mobile phase are displaced by the molecules of various atranes when they are sorbed onto the surface of the stationary phase. At the same time, for one of these compounds the slope differs when different polar modifiers are compared. This is in agreement with the different polarities of the modifiers. For example, one molecule of phenylsilatrane displaces, on average, 1.5 molecules of dioxane or 2.5 molecules of chloroform from the surface of Zorbax CN.

It is interesting that despite the similar b values observed for various solutes in our experiments, a correlation between a and b exists, which resembles that[6,7] observed in reversed-phase chromatography for various classes of compounds:

$$a = b_0 + b_1 b \tag{4}$$

The parameters of eqn. 4 are given in Table V. The presence of such a correlation signifies that the log k' *vs.* log C plots for different compounds are distributed fanwise and, when extrapolated to large C values, intersect in the vicinity of a point with the coordinates $\log k' = b_0$ and $\log C = -b_1$.

The k' values for some organo-silicon and -boron derivatives of amino alcohols in the reversed-phase mode on two stationary phases are summarized in Table VI. Analysis of the data also demonstrates certain patterns in retention behaviour, some being similar to those observed in GLC. For example, the introduction of a methyl or phenyl substituent into the atrane ring, as well as the introduction of additional methylene groups, leads to increased retention, *i.e.*, the influence of these structural features is the opposite of that on k' on polar Zorbax CN or on $\delta I_{\mathrm{N}\rightarrow\mathrm{M}}$ in GLC.

According to current notions, retention in the reversed-phase (RP) mode is governed primarily by hydrophobic interactions. Many structural parameters, *e.g.*, number of carbon atoms, connectivity indices, molecular polarizabilities, hydrophobic surface areas, partition coefficients, etc., have been used to describe hydrophobicity and retention[8–13]. A very popular approach is based on the correlations between Rekker's log P values (found experimentally or calculated[14]) and log k' values. We observed a similar regularity for atranes. The calculated sums of Rekker's f_i constants for substituents in atranes (Table VI) are correlated with the experimental capacity factors in a RP system consisting of Zorbax ODS and aqueous acetonitrile:

$$\log k' = -0.134 + 0.257\Sigma f_i \tag{5}$$

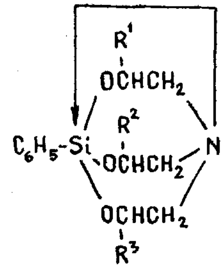
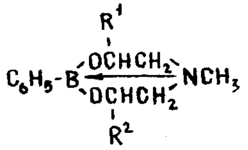
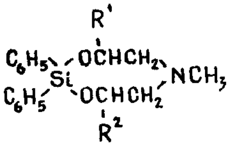
The correlation coefficient is 0.96, the standard error of approximation being 0.1. The accuracy of the model is sufficient for qualitative interpretation of chromatograms and preliminary evaluation of solvent composition for separation of compounds having a given set of substituents.

At the same time, eqn. 5 is based on the assumption that substituents do not influence the hydrophobicity and/or polarity of the atrane nucleus. It follows from the liquid chromatography data given above, as well as from earlier GC work, that such an assumption oversimplifies the actual influence of the chemical structure on retention. Moreover, it is clear that intramolecular interactions in the class of compounds studied significantly interfere with their ability to undergo intermolecular interactions. For this reason, log k' should be considered not only in relation to substituent hydrophobicity but also in relation to the influence exerted by substituents on the specific properties of atranes. The latter factors are of special importance in GLC, and therefore some analogy between GLC and reversed-phase HPLC behaviour is possible. If we consider only general aspects of retention mechanisms involved in these two modes of chromatography, it can be claimed that two factors mainly determine the chromatographic behaviour of chemical compounds both in GLC and RPLC: *viz.*, the size of the solute molecules and their polarities.

We believe that information on both these factors is provided by GLC data

TABLE III

RELATIONSHIP BETWEEN CAPACITY FACTORS OF AMINO ALCOHOL DERIVATIVES AND THE MOBILE PHASE COMPOSITION

Compound No.	*Structure*	*R^1*	*R^2*	*R^3*	*Dioxane (%, v/v) in hexane*						
					10	*15*	*20*	*25*	*30*	*40*	*50*
13		H	H	H	14.6	8.9	6.1	4.3	3.2	1.9	1.5
14		CH_3	H	H	9.1	6.0	4.2	3.1	2.4	1.4	1.2
15		CH_3	CH_3	H	5.1	3.5	2.6	2.0			
					5.5	3.8	2.8	2.1	1.6	1.0	0.9
					5.8	3.9	2.9	2.2	1.7	1.1	
16		CH_3	CH_3	CH_3	3.4	2.5	1.9				
								1.5	1.2	0.8	0.7
					3.6	2.6	2.0				
27		CH_3	CH_3	–	4.2		2.3		1.1	0.7	0.5
28		H	H	–	7.4		2.5		1.6	1.1	0.8

and therefore these data can be used to predict reversed-phase chromatographic behaviour. For example, the size of the molecule is the main factor responsible for retention on non-polar stationary phases in GLC, and therefore retention indices on such phases, *e.g.*, Apiezon, contain information on molecule size, at least for relatively large molecules. If two solutes have similar functional groups, the one which has the larger retention index on Apiezon is expected to be retained more strongly in RPLC. On the other hand, increasing solute polarity tends to increase retention in GLC and decrease sorption in RPLC. To evaluate the conditional chromatographic polarity of the solute several generally accepted parameters can be used. One of them is the well known ΔI value corresponding to differences between the GLC retention indices for a given compound on polar and non-polar stationary phases. Therefore the correlation between log k' and GLC parameters can be expressed by

$$\log k' = a_0 + a_1 I_A + a_2 \cdot \Delta I_C \qquad (6)$$

where I_A is the GLC retention index on Apiezon and ΔI_C is the ΔI value for OV-225–Apiezon L[1–3].

Diastereomer ratio	*Chloroform (%, v/v) in hexane*								*Diastereomer ratio*
	20	*25*	*30*	*40*	*50*	*60*	*80*	*100*	
	14.1	7.7	4.5	2.1	1.2	0.8	0.4	0.3	
	7.7	4.4	2.6	1.3	0.8	0.5	0.3	0.2	
1.16	3.7	2.3	1.4						1.13
1.00	3.9	2.4	1.5	0.8	0.5	0.4	0.3	0.2	2.23
2.25	4.5	2.6	1.6						1.00
2.62	1.8								
		1.2	0.8	0.4	0.3	0.3			
1.00	1.9								

Undoubtedly, I_A is affected not only by molecule size. Therefore we have introduced for the class of compounds under discussion a new parameter, I_H, which takes into account the skeletal atoms of the solute molecule and can be regarded as the "molecule size contribution" of the retention index

$$I_H = 100(n_C + n_N + n_O) \qquad (7)$$

where n_C, n_N, n_O are the number of carbon, nitrogen and oxygen atoms contained in the solute molecule; 100 is a scaling factor used to adjust I_H to the retention index scale.

The other way to express solute polarity is to use the $\delta I_{N \rightarrow M}$ parameter[1-3] which is specific for the class of solutes studied. It is the difference between experimentally measured I values and retention indices calculated on the basis of an additive scheme, and reflects "the excessive chromatographic polarity" of the solute due to the formation of the intramolecular N → M bond. I_H and $\delta I_{N \rightarrow M}$ can be used in the following

TABLE IV

PARAMETERS OF EQN. 3

Compound No. (Table III)	*Dioxane*					*Chloroform*				
	a	b	r	σ^*	F	a	b	r	σ^*	F
13	2.68	−1.48	0.997	0.03	812	4.44	−2.55	0.999	0.03	1687
14	2.32	−1.33	0.996	0.03	692	3.95	−2.37	0.998	0.03	1051
15	1.91	−1.15	0.993	0.03	1171	3.29	−2.09	0.992	0.05	705
16	1.62	−1.05	0.992	0.03	554	2.88	−2.01	0.999	0.01	3354

* σ = Standard error of estimate.

TABLE V

PARAMETERS OF EQN. 4

r = Correlation coefficient; F = F-criterion.

Polar modifier	b_0	b_1	r	F
Dioxane	−0.88	−2.41	0.999	1498
Chloroform	−2.47	−2.71	0.993	152

retention models

$$\log k' = a_0 + a_1 I_H + a_2 \cdot \Delta I_C \tag{8}$$

$$\log k' = a_0 + a_1 I_H + a_2 \cdot \delta I_{N \to M} \tag{9}$$

where $\delta I_{N \to M}$ is the difference between the experimental and calculated retention indices on OV-225.

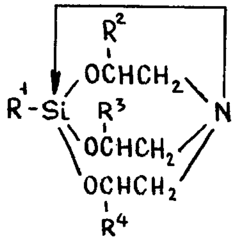
The parameters for eqns. 6, 8, 9 are given in Table VII. It is seen that eqn. 9 provides a satisfactory description of the relationship between GLC and HPLC retention data. The a_0 values in the three equations are very low, signifying that the hypothetical solute with $I_H = I_A = \Delta I_C = \delta I_{N \to M} = 0$ would be retained only negligibly in reversed-phase chromatography, in accord with the generally held ideas on the retention mechanism. The coefficients a_1 for solute size parameters I_H and I_A are positive and the coefficients a_2 for polarity parameters ΔI_C and $\delta I_{N \to M}$ are negative, in accord with the rôle of these factors in RPLC. The coefficients a_1 for I_H are similar in eqns. 8 and 9, and the values of a_2 for ΔI_C are similar in eqns. 6 and 8. This suggests that eqns. 6, 8, 9 provide, to a certain extent, a separation of the total retention effect into components corresponding to individual types of molecular interactions.

The diastereomers of atranes can also be resolved by HPLC. The data in Tables II and III show that the ratio of the peak areas for 1-phenyl-3,7,10-trimethylsilatrane diastereomers is close to that theoretically expected. Some variations in diastereomer ratios found in the presence of different polar modifiers are due to the fact that the peaks could not be resolved completely in all cases. The diastereomer ratio for 1-phenyl-3,7-dimethylsilatrane also corresponds to that theoretically expected. It is interesting that the order of diastereomer elution depends on the type of polar modifiers in normal-phase HPLC. For example, the peak of diastereomer "a" which is the first to be eluted on all GLC stationary phases[1] is the third eluted when isopropanol or dioxane is used and second when chloroform is used (Fig. 6).

The separation of diastereomers with phenyl groups in positions 3, 7 (compounds 10 and 18) is achieved more easily than in GLC, where such compounds are strongly retained. At the same time, the ratio of the peak areas evidences that the diastereomer ratio differs from that theoretically expected. A similar effect for 4,4-disubstituted atranes was observed previously in the case of GLC[1]. One of these compounds (No. 22, Table II) has also been separated by HPLC, and its diastereomer ratio practically coincides with the value found in GLC. The chains of the atrane skeleton also influence the diastereomer composition. For example, the introduction

TABLE VI

CAPACITY FACTORS OF ALKANOLAMINE DERIVATIVES IN REVERSED-PHASE CHROMATOGRAPHY

Compound No.	*General formula*	*Substituents*				*k' on Zorbax ODS Acetonitrile–water (50:50)*	*k' on MicroPak CH-10 Acetonitrile–water (32:68)*	*Σf_i*	*I_B*
		R^1	*R^2*	*R^3*	*R^4*				
9		$CH_2=CH$	C_6H_5	H	H	3.3		2.82	1800
10		$CH_2=CH$	C_6H_5	C_6H_5	H	9.4		4.71	2400
						12.2			
						12.9			
13		C_6H_5	H	H	H	2.4	2.1	1.89	1600
14		C_6H_5	CH_3	H	H	3.3	4.2	2.59	1700
15		C_6H_5	CH_3	CH_3	H	4.8	8.7	3.29	1800
16		C_6H_5	CH_3	CH_3	CH_3		18.8		1900
17		C_6H_5	C_6H_5	H	H	7.2		3.77	2200
18		C_6H_5	C_6H_5	C_6H_5	H	21.3		5.70	2800
						29.4			
						30.1			
19		C_6H_5O	H	H	H	2.4		1.46	1700
20		$C_6H_5CH_2CH_2$	H	H	H	3.9		2.95	1800
21		$C_{10}H_7$	H	H	H	5.2			2000

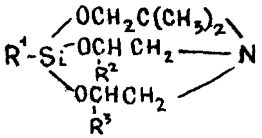
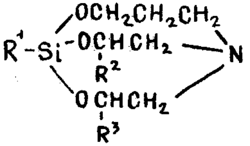
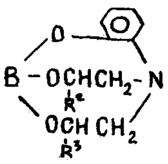
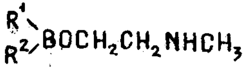
22		C_6H_5	CH_3	CH_3	–	7.5 9.3	17.8 24.5	4.69	2000
26		C_6H_5	CH_3	CH_3	–	23.5 25.4 33.3			1900
30		–	H	H	–	1.7			1400
31	 $R^1R^2BOCH_2CH_2NHCH_3$	C_6H_5	C_6H_5	–	–	9.8			1900

TABLE VII

PARAMETERS OF EQNS. 6, 8, 9

Equation	a_0	a_1	a_2	r	σ	F
6	−0.218	0.000627	−0.000547	0.80	0.22	7
8	−0.641	0.000952	−0.000504	0.87	0.17	13
9	−0.864	0.000838	−0.000176	0.98	0.07	68

of an additional methylene group into the atrane skeleton, converting it into homosilatrane 26, leads to the ratio 1:1:8 instead of 1:1:2 was observed for the parent compound. Compound 29 has asymmetric carbon and silicon atoms. The separation that has been achieved is, perhaps, the first reported case of an HPLC separation of isomers containing a chiral silicon.

If we compare the relative retention values with the relative amounts of the diastereomers, it is found that readily separable compounds tend to have "abnormal"

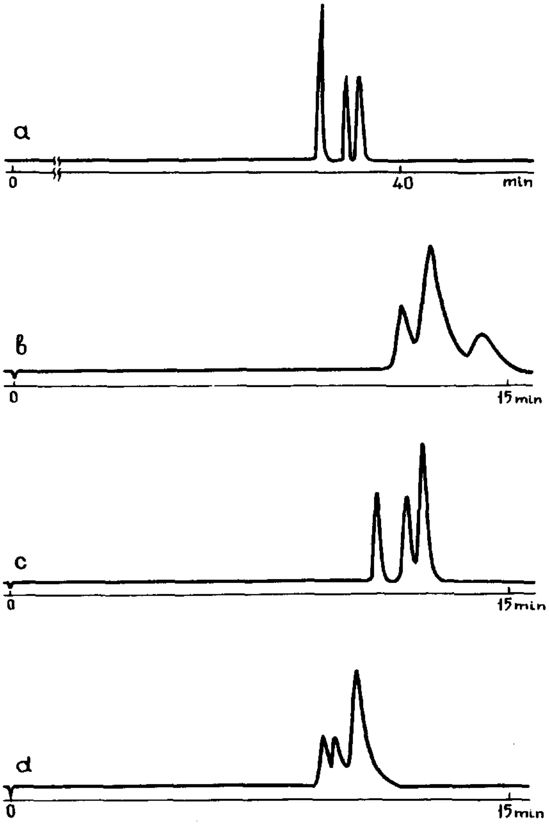


Fig. 6. Separation of 1-phenyl-3,7-dimethylsilatrane diastereomers: (a) GLC capillary column with OV-17; (b) HPLC on Zorbax CN, chloroform–hexane (1:4); (c) HPLC on Zorbax CN, dioxane–hexane (3:17); (d) HPLC on Zorbax CN, isopropanol–hexane (1:9).

diastereomer ratios, whereas compounds which have the theoretically expected ratio are very difficult to separate. We believe that a specific composition and arrangement of substituents is responsible for both these factors: enhanced selectivity of isomer formation during chemical synthesis and enhanced selectivity during interaction with the chromatographic phases.

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