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CHROMATOGRAPHY OF ORGANOMETALLIC AND ORGANOMETALLOIDAL DERIVATIVES OF AMINO ALCOHOLS

I. RETENTION INDICES OF SILATRANES

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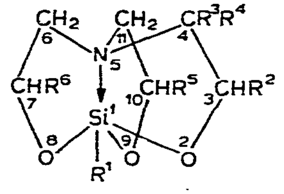
SUMMARY

The applicability of gas chromatography for the resolution of silatranes at 200–250° has been demonstrated. Retention indices were measured for 48 compounds of this class. Remarkably high values of the retention indices (I) and ΔI were found to be characteristic of all of the substances studied, which could not be accounted for on the basis of formal analysis of structural fragments. The relationship between the observed retention characteristics and silatrane structure was examined. A correlation was established between the retention characteristics and the properties of substituents attached to the silicon atom, permitting the assessment of dipole moments and induction constants. It was found that the extremely strong interaction of silatrane molecules with the stationary phase was due to the influence exerted by the transannular N → Si bond. The mean contribution of the structural fragment $\equiv N \rightarrow Si \equiv$ to I was 430, 640 and 900 units on Apiezon L, OV-17 and OV-225, respectively. The separation of diastereomeric C-substituted silatranes was demonstrated and the order of elution is discussed. The character of changes in retention caused by the introduction of methyl groups in the α-position with respect to oxygen atoms indicates that the high I values are due mainly to the interaction of oxygen atoms with the acceptor groups of the stationary phase.

INTRODUCTION

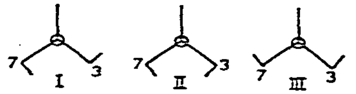
In recent years there has been a rapid increase in the study of the synthesis and properties of organo-element derivatives of amino alcohols, especially the cyclic organosilicon ethers of triethanolamine, the so-called silatranes[1]. Several methods have been proposed for their synthesis, and the IR and NMR spectra, dipole moments and other physico-chemical and biological properties of these compounds have been studied[2–4]. X-Ray analysis data[5] revealed that silatranes (2,8,9-trioxa-5-aza-1-silatricyclo[3,3,3^{1,5}] undecanes) exist as intramolecular complexes with a transannular N → Si bond:



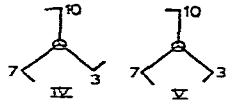
where R^1 = organic radical;
R^2–R^6 = H or CH_3

These compounds have high melting and boiling points and are characterized by high polarity. This is probably the reason why there have been no reports in the literature on gas–liquid chromatography (GLC) being applied to the study of silatranes. We have found that many representatives of this class of compounds possess fairly high thermal stability and volatility, and are stable under the conditions applied in GLC up to 250°.

The molecules of 3,7-di- and 3,7,10-trimethylsilatranes carry two and three asymmetric centres, respectively, and exist in the following diastereomeric forms[6]:

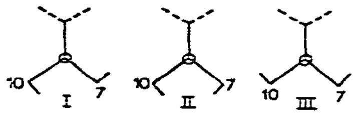


3,7-disubstituted



3,7,10-trisubstituted

4,4,7,10-Tetrasubstituted derivatives, in analogy with 3,7-disubstituted silatranes, form three diastereomers:



It was of interest to investigate the applicability of gas chromatography to the resolution of these diastereomers. Moreover, using the values of I found for this group of compounds, one can draw inferences as to the nature of the strong interaction between silatranes and the molecules of the stationary phase. If the retention of silatranes is largely determined by the interaction of oxygen atoms with the stationary phase, it would be expected that the methyl substituents in positions 3, 7 and 10 will affect substantially the I and ΔI values of silatranes.

This paper reports the results obtained in a study of the I values of C- and Si-substituted silatranes; a discussion of the possible reasons for their retention is presented. The resolvability of diastereomers of C-substituted silatranes is demonstrated and the order of elution is discussed.

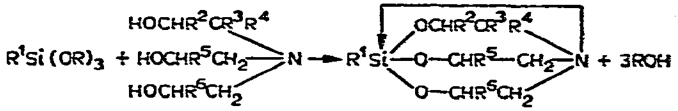
EXPERIMENTAL

I values were measured on Hewlett-Packard Model 7620 and Chrom-4 chromatographs at 200°. Several less volatile substances were chromatographed at 250°.

Apiezon L (A), OV-17 (B), OV-225 (C) and Carbowax 20M (D) were used as stationary phases. The solid support was 80–100-mesh Chromosorb W HP. Glass columns A, B and C (1.2 m in length) with I.D. 2 mm (HP 7620) or 3 mm (Chrom-4) were employed. Column D was made of stainless steel (I.D. 2.2 mm, length 2.4 m). The column efficiency with respect to methylsilatrane was above 1500 theoretical plates. Samples (1–10% solutions in acetone) were injected using Hamilton and OKBA microsyringes, the volumes ranging from 0.2 to 0.5 µl. *n*-Alkanes (C_{12}–C_{36}) were used as reference compounds for the measurement of I values. To measure I values exceeding 3600, extrapolation of the plot of the logarithm of the retention volume *versus* the number of carbon atoms in the *n*-alkanes was used. The values of ΔI for polar stationary phases were determined with respect to Apiezon L.

The silatranes used had been synthesized by conventional methods[1–4], and their characteristics were in agreement with the literature data.

C-Substituted silatranes were obtained by treating organotrialkoxysilanes with the appropriate trialkanolamines according to the scheme



The reaction was performed in xylene in the presence of catalytic amounts of potassium hydroxide with continuous removal of the alkanol formed during the process. Compounds 9 and 16 were obtained by heating the initial reagents for a short period in the presence of catalytic amounts of a saturated alcoholic solution of sodium ethoxide. The products were purified by recrystallization (from benzene, Nos. 13 and 16; from *n*-heptane, Nos. 2, 3, 4, 7 and 9; from *n*-hexane, Nos. 6 and 12; from *n*-pentane, No. 11; from *n*-pentane–diethyl ether, Nos. 8 and 14), freezing from diethyl ether solution (Nos. 10 and 15), distillation (No. 5), and distillation with subsequent crystallization from light petroleum–*n*-hexane (No. 1).

The melting points and yields of new compounds are listed in Table I, which also includes the data on two already known silatranes, the melting points of which were at variance with those reported in the literature. The characteristics of the other compounds, 1,3-dimethylsilatrane, 1-phenyl-3,7-dimethylsilatrane and 3,7,10-trimethylsilatrane, were in agreement with the reported data[7–10].

In addition to packed columns, we used a stainless-steel capillary column (50 m × 0.25 mm) coated with OV-17 and a glass capillary column (20 m × 0.2 mm) coated with SE-30 for diastereomer resolution.

RESULTS AND DISCUSSION

Preliminary investigations have shown that silatranes, despite their high melting and boiling points, can be converted into the vapour phase from acetone solutions by using chromatograph injection port temperatures of 250–280°. No evidence of decomposition was found when using either stainless-steel or glass injection ports. Similarly, we concluded that silatranes could be chromatographed

TABLE I

SYNTHESIZED SILATRANES

No.	*R^1*	*R^2*	*R^3*	*R^4*	*R^5*	*R^6*	*Yield (%)*	*M.p. (°C)*
1	C_2H_5O	CH_3	H	H	H	H	60	65–66 (174/2.5)*
2	C_6H_5	CH_3	H	H	H	H	63	95–96**
3	CH_3	CH_3	H	H	CH_3	H	62	119–121
4	CH_3	CH_3	H	H	CH_3	CH_3	87	133–135
5	iso-C_3H_7	CH_3	H	H	CH_3	CH_3	61	42–43 (113/3)*
6	C_2H_5O	CH_3	H	H	CH_3	CH_3	54	85–86***
7	C_6H_5	CH_3	H	H	CH_3	CH_3	93	135–136
8	CH_3	H	CH_3	CH_3	CH_3	CH_3	69	63
9	$ClCH_2$	H	CH_3	CH_3	CH_3	CH_3	72	145–146
10	$CH_2{=}CH$	H	CH_3	CH_3	CH_3	CH_3	54	96–97
11	cyclo-C_3H_5	H	CH_3	CH_3	CH_3	CH_3	68	84
12	CH_3O	H	CH_3	CH_3	CH_3	CH_3	59	108–109
13	C_6H_5	H	CH_3	CH_3	CH_3	CH_3	70	117.5–119
14	$C_6H_5CH_2$	H	CH_3	CH_3	CH_3	CH_3	61	127–128
15	3-ClC_6H_4	H	CH_3	CH_3	CH_3	CH_3	84	123–124
16	4-BrC_6H_4	H	CH_3	CH_3	CH_3	CH_3	82	163–164

* Values in parentheses are boiling points (°C/mm).

** 85–87° according to ref. 7.

*** 81.7–82.2° according to ref. 10.

on columns made of either of these materials, and a flame-ionization detector could be safely used. We observed no anomalous reaction of the detector towards silatranes.

I and *ΔI* values found for silatranes are given in Table II. It is apparent that *I* and, in particular, *ΔI* are characterized by extremely high values which cannot be accounted for by the mere analysis of the structural fragments of silatranes. For instance, *ΔI* found for phenoxysilatrane on OV-225 is 1517 units, whereas *ΔI* values for McReynolds polarity test compounds never exceed 492 units (nitropropane). Thus although the molecules of silatranes carry no functional groups that possess high polarity, these substances behave chromatographically like extremely polar compounds.

We have attempted to calculate the *I* values of silatranes by summing the increments corresponding to individual structural fragments. The values of the increments used were taken from retention studies reported in the literature for various organic and organosilicon compounds which contain the necessary structural fragments[11–14]. The results of these calculations are summarized in Table III. It is evident that the additive calculations result in significant underestimations of *I* values (amounting to 1200 units on OV-225). The observed difference between the experimental and calculated values is apparently due to considerably altered properties of some structural fragments as a result of N → Si transannular bonding. Conversely, the calculation of *I* values for other nitrogen- and oxygen-containing organosilicon compounds that lack this kind of bonding with recourse to the same increments usually results in values slightly higher than the experimental values. It should be pointed out that the discrepancy between the calculated and experimentally found *I* values is correlated with the effective electronegativity of the substituents attached to

TABLE II

RETENTION PARAMETERS OF SILATRANES

No.	R^1	*Stationary phase*						
		A	*B*		*C*		*D*	
		I	*I*	*ΔI*	*I*	*ΔI*	*I*	*ΔI*
1	H	1487	1883	396	2597	1110		
2	CH_3	1387	1705	318	2142	755	2258	871
3	C_2H_5	1462	1772	310	2187	725	2294	832
4	*n*-C_4H_9	1631	1954	323	2327	696	2440	809
5	*n*-C_5H_{11}	1721	2054	333	2419	698	2532	811
6	cyclo-C_3H_5	1608	1984	376	2439	831	2558	950
7	cyclo-C_6H_{11}	1901	2235	334	2602	701	2747	846
8	$CH_2{=}CH$	1522	1915	393	2463	941	2580	1058
9	CH_3O	1603	2061	458	2774	1171	2883	1280
10	C_2H_5O	1614	2060	446	2705	1091	2808	1194
11	*n*-C_3H_7O	1689	2140	451	2753	1064	2858	1169
12	iso-C_3H_7O	1599	2018	419	2583	984	2672	1073
13	*n*-C_4H_9O	1780	2240	460	2838	1058	2943	1163
14	iso-C_4H_9O	1724	2172	448	2744	1020	2849	1125
15	*tert.*-C_4H_9O	1602	2061	459	2771	1169	2888	1286
16	*n*-$C_5H_{11}O$	1877	2341	464	2938	1061	3042	1165
17	C_6H_5	2242	2634	392	3171	929		
18	$C_6H_5CH_2CH_2$	2160	2588	428	3200	1040	3335	1174
19	*p*-$CH_3C_6H_4$	2197	2645	448	3332	1135		
20	*o*-ClC_6H_4	2267	2730	463	3457	1190		
21	*p*-ClC_6H_4	2343	2786	443	3547	1201		
22	α-$C_{10}H_7$	2718	3240	522	4125	1407		
23	C_6H_5O	2288	2955	667	3805	1517		
24	*o*-$CH_3C_6H_4O$	2307	2949	642	3756	1449		
25	*m*-$CH_3C_6H_4O$	2527	3211	684	4021	1494		
26	*p*-$CH_3C_6H_4O$	2384	3045	661	3885	1501		
27	2-iso-C_3H_7-5-CH_3-C_6H_3O	2396	3069	673	3781	1385		
28	*p*-ClC_6H_4O	2521	3192	671	4057	1536		
29	β-$C_{10}H_7O$	2919	3211	292				

TABLE III

RESULTS OF ADDITIVE CALCULATIONS OF RETENTION INDICES OF SILATRANES

R^1	*Stationary phase*					
	A		*B*		*C*	
	$I_{calc.}$	$I_{exp.} - I_{calc.}$	$I_{calc.}$	$I_{exp.} - I_{calc.}$	$I_{calc.}$	$I_{exp.} - I_{calc.}$
H	970	517	1180	703	1420	1177
CH_3	1070	317	1280	425	1520	622
CH_3O	1140	463	1470	591	1770	1004
C_2H_5O	1190	414	1510	550	1810	895
n-C_4H_9O	1380	400	1680	560	1970	868
iso-C_4H_9O	1360	363	1660	512	1940	804
tert.-C_4H_9O	1310	292	1620	441	1900	871
C_6H_5	1650	592	1930	704	2300	871
C_6H_5O	1760	528	2260	695	2620	1185
o-$CH_3C_6H_4O$	1830	477	2340	609	2710	1046

the silicon atom (Fig. 1). The difference between the calculated and experimental results increases with increasing electronegativity; this pattern is also paralleled by the increasing stability of the N → Si bond.

The high retention characteristics observed for silatranes are indicative of strong interactions between their molecules and the molecules of the stationary phase. In addition to non-specific dispersion forces, at least two other types of intermolecular interactions may be involved in this effect. Firstly, silatrane molecules have fairly high dipole moments and are capable of orientational interaction with the molecules of the stationary phase. Further, interactions are possible (including hydrogen bonding) between several atoms in the molecules of silatranes and the stationary phase, which carry sufficiently high excessive charges. Such interactions appear to be plausible, taking into account the fact that N → Si transannular bonding leads to higher negative charges on the oxygen atoms of the silatrane rings than those on the oxygen atoms of the alkoxysilanes that were used for the determination of increments.

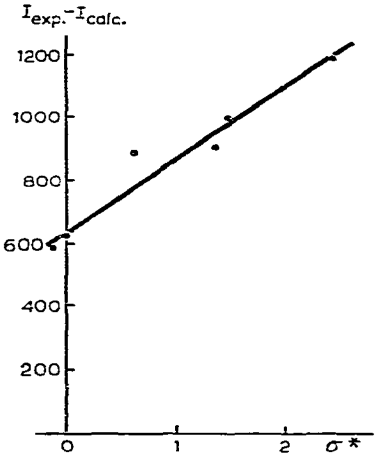


Fig. 1. Dependence of $I_{exp.} - I_{calc.}$ values on induction constants of substituent in position 1.

The role of dipole–dipole interactions can be demonstrated by examining the relationship between the retention values and dipole moments of solutes, whereas the effect of the local excessive charges can be assessed by comparing the retention of molecules differing in the spatial environment of the appropriate atoms.

We have found that the dipole moments (μ) and ΔI values observed on OV-225 are related by the equation

$$\Delta I = -1862 + 364\mu \tag{1}$$

the correlation coefficient being equal to 0.91. This equation permits the determination of dipole moments on the basis of ΔI values with a mean square deviation from the experimental data of less than 5% (Table IV).

On the other hand, the retention characteristics of silatranes are, beyond any doubt, influenced by spatial factors. Thus, comparison of the I values of substances

TABLE IV

DIPOLE MOMENTS OF SILATRANES

R^1	μ_{chrom}	μ_{CHCl_3} (ref. 15)
CH_3	7.18	7.57
C_2H_5	7.10	7.06
$CH_2=CH$	7.70	7.38
C_2H_5O	8.11	8.31
C_6H_5O	9.28	9.23
H	8.18	8.00
m-$CH_3C_6H_4O$	9.21	9.01
2-iso-C_3H_7-5-$CH_3C_6H_3O$	8.91	8.35
p-ClC_6H_4O	9.33	10.09

25 and 27 (Table II) revealed that the latter substance is retained considerably more weakly than substance 25, although its molecule contains more carbon atoms; the difference in the retentions of this pair of compounds increases with increasing polarity of the stationary phase. By analogy with the above example, compounds 12, 14 and 24 show weaker retentions than compounds 11, 13 and 26, respectively.

The influence of substituents in position 1 of the silatrane ring on retention characteristics may be described quantitatively with the help of the modified Taft equation:

$$I = a_0 + a_1 n_c + a_2 \sigma^* \tag{2}$$

$$\Delta I = a_0 + a_1 \sigma^* \tag{3}$$

$$I = a_0 + a_1 n_c + a_2 \sigma^* + a_3 E_s^0 \tag{4}$$

$$\Delta I = a_0 + a_1 \sigma^* + a_2 E_s^0 \tag{5}$$

where n_c is the number of carbon atoms in the substituent, σ^* is the Taft induction constant[16] and E_s^0 is a steric constant[16].

Equations and criteria that characterize the correlation were obtained by the method of the least squares and are summarized in Table V. It is apparent that there is a good correlation between I, the number of carbon atoms in the substituent and inductive and steric properties. In all instances the coefficient of σ^* is positive and increases with the increasing polarity of the stationary phase. Consequently, I and ΔI values increase with increasing electronegativity of the substituent in position 1, the size of the increase being dependent on the polarity of the stationary phase. The degree of correlation diminishes upon extending the range of substances covered by a single equation, particularly on polar stationary phases. This indicates that the modified Taft equations used fail to contain all of the possible factors that affect the interaction between the molecules of silatranes and the stationary phase.

It must be pointed out that the coefficients in the equations describing ΔI values can be approximated not only by the appropriate processing of experimental data, but also by subtraction of the corresponding coefficients in equations describing I. The coefficient of n_c found by this procedure has a low absolute value and is statistically nsignificant. The retention models presented above can also be employed for the

TABLE V

MODELS OF SILATRANE RETENTION

r = Coefficient of multiple correlation; F = coefficient of determination.

Group of silatranes	*Column*	*Equation*	r	σ	F
1-Alkylsilatranes	A	$I = 1300 + 87.5n_c + 133\sigma^*$	0.99	1	12,000
	B	$I = 1608 + 96.7n_c + 306\sigma^*$	0.99	1	11,000
	C	$I = 2062 + 80.7n_c + 397\sigma^*$	0.99	4	370
1-Alkyl- and 1-alkoxy-silatranes	A	$I = 1327 + 77.3n_c + 104\sigma^*$	0.98	26	90
	B	$I = 1641 + 82.6n_c + 194\sigma^*$	0.99	30	130
	C	$I = 2116 + 61.3n_c + 351\sigma^*$	0.98	47	110
	B − A	$\Delta I = 329 + 90.7\sigma^*$	0.99	9	450
	C − A	$\Delta I = 739 + 247\sigma^*$	0.98	31	260
Various silatranes (substances 1–29)	A	$I = 1284 + 98.2n_c + 95.9\sigma^*$	0.92	89	40
	B	$I = 1471 + 130n_c + 285\sigma^*$	0.85	205	20
	C	$I = 2044 + 106n_c + 341\sigma^*$	0.89	160	30
1-Alkyl- and 1-alkoxy-silatranes	A	$I = 1308 + 98.8n_c + 114\sigma^* + 121E_s^\circ$	0.99	14	200
	B	$I = 1616 + 112n_c + 202\sigma^* + 152E_s^\circ$	0.99	19	200
	C	$I = 2085 + 93.6n_c + 369\sigma^* + 175E_s^\circ$	0.99	27	210
	B − A	$\Delta I = 323 + 94\sigma^* + 3.75E_s^\circ$	0.99	6	370
	C − A	$\Delta I = 775 + 255\sigma^* + 92E_s^\circ$	0.99	12	760
Various silatranes (substances 1–29)	A	$I = 1304 + 115n_c + 96.96\sigma^* + 150E_s^\circ$	0.98	45	114
	B	$I = 1514 + 166n_c + 2876\sigma^* + 324E_s^\circ$	0.95	121	45
	C	$I = 2074 + 131n_c + 342\sigma^* + 231E_s^\circ$	0.95	121	40

preliminary assessment of the inductive influence of substituents in position 1; σ^* values in this instance are determined chromatographically, the mean error being *ca.* 30%.

It is noteworthy that the value of a_0 varies only insignificantly when different groups of substances are compared. However, this value tends to increase with increasing polarity of the stationary phase. In physical terms, a_0 denotes the I value of a hypothetical silatrane that is characterized by the following structural parameters: $n_c = 0$, $\sigma^* = 0$ and $E_s^0 = 0$. For the naturally occurring methylsilatrane, $n_c = 1$, $\sigma^* = 0$ and $E_s^0 = 0$. I values on stationary phases A, B and C are 1387, 1705 and 2142, respectively, which are in good agreement with the values of a_0 in the corresponding equations. Similarly, ΔI values found for methylsilatrane and a_0 values of the equations describing ΔI values of Si-substituted silatranes appear to be related (323 and 775, 318 and 755). We can further subtract from a_0 the increments corresponding to the three groups $-OCH_2CH_2-$, which would result in the total value describing the contribution to I by the structural fragment $\equiv N \rightarrow Si \equiv$. These contributions on stationary phases A, B and C are 430, 640 and 900 I units, respectively. The values obtained are in good agreement with the mean deviation between calculated and experimental values (Table III) and therefore they may serve for objective evaluations of the contribution made by the structural fragment $\equiv N \rightarrow Si \equiv$ to the retention characteristics.

I and ΔI values found for C-substituted silatranes are summarized in Table VI. It is evident that in most instances two or three peaks (designated in Table VI as a, b and c) correspond to any particular compound, which may be the result of partial or complete resolution of diastereomers. With regard to the number of substituents attached to carbon atoms, silatranes capable of forming diastereomers fall into three groups. Typical chromatograms of representatives of each group are depicted in Fig. [illegible].

TABLE VI

RETENTION PARAMETERS OF C-SUBSTITUTED SILATRANES

R^1	*Diastereomer peak*	R^2	R^3	R^4	R^5	R^6	*Stationary phase*						
							A	*B*		*C*		*D*	
							I	*I*	*ΔI*	*I*	*ΔI*	*I*	*ΔI*
CH_3		CH_3	H	H	H	H	1380	1672	292	2077	697	2163	789
C_6H_5		CH_3	H	H	H	H	2075	2494	419	3155	1080		
C_2H_5O		CH_3	H	H	H	H	1584	2020	436	2631	1047		
CH_3	a	CH_3	H	H	CH_3	H	1357	1637	280	2004	647	2066	709
	b + c						1381	1672	291	2041	660	2107	720
C_6H_5	a	CH_3	H	H	CH_3	H	2038	2432	394	3059	1021		
	b + c						2067	2458	391	3082	1015		
H	d	CH_3	H	H	CH_3	CH_3	1569	1954	385	2764	1195		
	e						1618	2033	415	2869	1251		
CH_3	d	CH_3	H	H	CH_3	CH_3	1365[*]	1597	232	1928	563	1966	601
	e						1365[*]	1630	265	1965	600	2000	635
iso-C_3H_7	d	CH_3	H	H	CH_3	CH_3	1410	1637	227	1894	484	1903	493
	e						1441	1680	239	1945	504	1962	521
C_2H_5O	d	CH_3	H	H	CH_3	CH_3	1552	1915	363	2455	903		
	e						1596	1957	361	2491	901		
C_6H_5	d	CH_3	H	H	CH_3	CH_3	1991	2361	370	2945	954		
	e						2022	2397	375	2980	958		
CH_3	a		CH_3	CH_3	CH_3	CH_3	1514[*]	1767[*]	253	2102	588		
	b						1514[*]	1767[*]	253	2142	628		
	c						1514	1767	253	2170	656		
$ClCH_2$	a	H	CH_3	CH_3	CH_3	CH_3	1869	2238	369	2850	981		
	b						1905	2298	393	2950	1045		
	c						1943	2367	424	3048	1115		
$CH_2=CH$	a	H	CH_3	CH_3	CH_3	CH_3	1651[*]	1929	278	2379	728		
	b						1651[*]	1953	302	2435	784		
	c						1651[*]	1983	332	2491	840		
cyclo-C_3H_5	a	H	CH_3	CH_3	CH_3	CH_3	1717[*]	1998	281	2368	651		
	b						1717[*]	2017	300	2407	690		
	c	H	CH_3	CH_3	CH_3	CH_3	1717[*]	2051	334	2459	742		
CH_3O	a	H	CH_3	CH_3	CH_3	CH_3	1743	2086	343	2703	960		
	b						1763	2117	354	2768	1005		
	c						1788	2154	366	2840	1058		
C_6H_5	a	H	CH_3	CH_3	CH_3	CH_3	2150	2513	363	3103	953		
	b						2176	2547	371	3176	1000		
	c						2199	2581	382	3251	1052		
$C_6H_5CH_2$	a	H	CH_3	CH_3	CH_3	CH_3	2090	2448	358	2896	806		
	b						2113	2489	376	2964	851		
	c						2138	2539	401	3040	902		
m-ClC_6H_4	a	H	CH_3	CH_3	CH_3	CH_3	2379	2752	373	3432	1053		
	b						2410	2793	383	3524	1114		
	c						2457	2844	387	3580	1123		
p-BrC_6H_4	a	H	CH_3	CH_3	CH_3	CH_3	2481	2838	357	3510	1029		
	b						2517	2902	385	3602	1085		
	c						2559	2973	414	3706	1147		

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[*] Overlapping of diastereomer peaks resulted in measurement error of about 10 units.

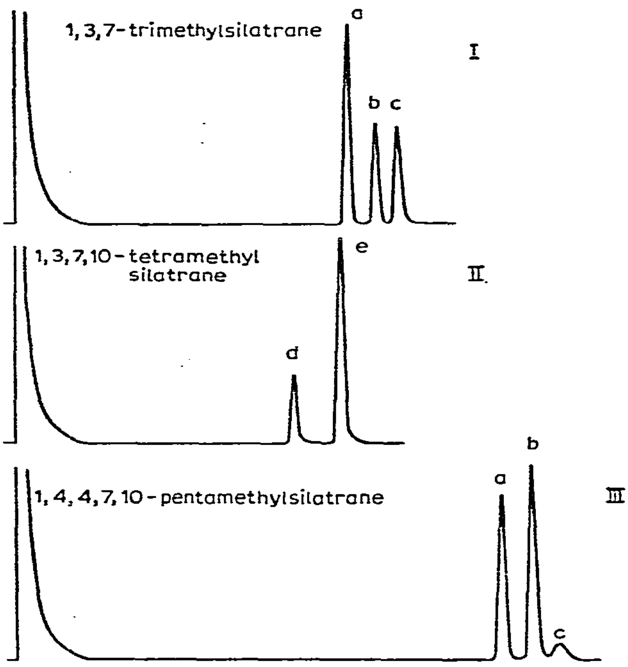

Fig. 2. Typical chromatograms of silatrane diastereomers obtained on the capillary column coated with OV-17.

3,7-Dimethyl-substituted silatranes on the relatively polar stationary phase OV-225 invariably yielded two peaks, the second peak being fairly broadened, which is indicative of partial resolution. The areas of the two peaks were in the ratio 1:1. Complete resolution of the three diastereomers of 3,7-dimethylsilatranes is attainable on the capillary column (Fig. 2, I). This results in the splitting of the second peak observed on the packed column into two and the areas of the three peaks observed (a, b and c) are in the ratio 2:1:1. A similar ratio of the amounts of diastereomers I, II and III in 3,7-dimethylsilatranes is also evidenced by PMR spectral data[6]. Consequently, peaks a, which are the first to elute, correspond to diastereomer I. We have undertaken the preparative isolation of individual fractions corresponding to peaks a and b + c. PMR spectral analysis of these fractions confirmed the concordance of peak a with diastereomer I and peak b + c with isomers II and III. Chromatography–mass spectrometry demonstrated the spectral identity of the substances in peaks a, b and c.

3,7,10-Trimethylsilatranes invariably yielded two peaks (d and e), the ratio of their areas being 1:3 (Fig. 2, II). This is consistent with PMR data[6] and permits peaks d and e to be assigned to diastereomers IV and V, respectively. In this instance also chromatography–mass spectrometry indicated the spectral identity of the peaks.

4,4,7,10-Tetramethylsilatranes are also expected to form three diastereomers, similar to I, II and III. In fact, the chromatography of compounds from this group resulted in three peaks, whose areas, however, had a ratio other than 2:1:1 (Table VII; Fig. 2, III). Peak b was the largest in all instances, whereas peak c was the smallest. We should point out that the area of peak c is inversely correlated with the size of

TABLE VII

DIASTEREOMER COMPOSITION OF C-SUBSTITUTED SILATRANES

Silatranes	*Ratio of peak areas*
1,3,7,10-Tetramethyl-	24:76
1-Isopropyl-3,7,10-trimethyl-	25:75
1,3,7-Trimethyl-	50:25:25
1-Phenyl-3,7-dimethyl-	50:25:25
1,4,4,7,10-Pentamethyl-	38:53:9
1-Methoxy-4,4,7,10-tetramethyl-	40:57:3
1-Vinyl-4,4,7,10-tetramethyl-	37:58:5
1-Chloromethyl-4,4,7,10-tetramethyl-	20:79:1
1-Phenyl-4,4,7,10-tetramethyl-	41:58:1

the substituent at the silicon atom. Chromatography–mass spectrometry indicated the spectral identity of the substances corresponding to peaks a, b and c, thus confirming their isomeric origin. Consequently, it can be concluded that in the presence of two methyl groups in position 4, the diastereomers are formed in proportions other than the theoretically expected ratio of 2:1:1. The type of substituent in position 1 is also likely to influence the ratio of isomers. We isolated small amounts of 1-cyclopropyl-4,4,7,10-tetramethylsilatrane diastereomers corresponding to peaks a and b. PMR spectral analysis of these samples demonstrated the assignment of peak b to diastereomer I. It was also established that peak a corresponds either to diastereomer II or III, or to a mixture of both. Consequently, an altered order of diastereomer elution is observed in this instance in comparison with 3,7-dimethylsilatranes. PMR spectral studies failed to resolve the problem of the assignment of peak c to any of the diastereomeric forms. Capillary column chromatography provided no evidence of any broadening of peak a, thus signifying that peak c is in fact a diastereomer, but not a contaminant of any kind that could be typically present in all investigated 4,4,7,10-tetramethylsilatranes.

The above results indicate that we have been successful in confirming the assignment of chromatographic peaks and structures to diastereomers I, IV and V. Resolution of diastereomers II and III is attainable in many instances using packed columns; capillary columns almost always give positive results. However, the order of elution of these substances has not yet been established and this aspect will be studied further.

We also carried out additive calculations of I values for C-substituted silatranes and compared the values obtained with the experimental values (Table VIII). As with Si-substituted silatranes, the difference between the calculated and experimentally found values increases with increasing electronegativity of the substituent at the silicon atom. However, following the introduction of methyl groups in the α-position with respect to oxygen atoms, this difference progressively decreases and with 3,7,10-trimethylsilatranes it amounts to only 55–65% of the initial value observed for α-unsubstituted analogues. The value of $I_{exp.} - I_{calc.}$ decreases by approximately 16% following the introduction of each successive methyl group in the α-position. Likewise, a comparison of C-unsubstituted silatranes with 3,7,10-trimethylsilatranes shows a decrease in ΔI by approximately 60 units following the introduction of each successive methyl group.

TABLE VIII

RESULTS OF ADDITIVE CALCULATIONS OF RETENTION INDICES

R^1	R^2	R^3	R^4	R^5	R^6	*Stationary phase*					
						A		*B*		*C*	
						$I_{calc.}$	$I_{exp.} - I_{calc.}$	$I_{calc.}$	$I_{exp.} - I_{calc.}$	$I_{calc.}$	$I_{exp.} - I_{calc.}$
CH_3	CH_3	H	H	H	H	1110	270	1320	352	1540	531
C_6H_5	CH_3	H	H	H	H	1690	385	1970	524	2320	835
CH_3	CH_3	H	H	CH_3	H	1140	217	1360	277	1560	444
C_6H_5	CH_3	H	H	CH_3	H	1720	318	2010	422	2340	719
H	CH_3	H	H	CH_3	CH_3	1080	489	1300	654	1480	1284
CH_3	CH_3	H	H	CH_3	CH_3	1180	185	1400	197	1580	348
C_2H_5O	CH_3	H	H	CH_3	CH_3	1350	202	1630	285	1870	584
C_6H_5	CH_3	H	H	CH_3	CH_3	1760	231	2050	311	2360	585
CH_3	H	CH_3	CH_3	CH_3	CH_3	1330	184	1540	227	1740	362
CH_3O	H	CH_3	CH_3	CH_3	CH_3	1450	293	1730	287	1990	713
C_6H_5	H	CH_3	CH_3	CH_3	CH_3	1910	240	2190	323	2520	583

An exception to this effect is provided by Si-unsubstituted silatranes, which even show a slight increase in ΔI on the introduction of methyl groups in positions 3, 7 and 10. Significant shielding of oxygen atoms by C-methyl groups presumably takes place only when there is also a substituent attached to silicon (*i.e.*, in the second α-position with respect to oxygen). It is noteworthy that these two α-positions differ in their chromatographic behaviour. The introduction of a methyl group in position 1 causes a greater reduction in ΔI than the introduction of methyl groups in positions 3, 7 and 10. For instance, ΔI on OV-225 decreases by 355 units on transition from silatrane to 1-methylsilatrane and by 632 units on transition from 3,7,10-trimethylsilatrane to 1,3,7,10-tetramethylsilatrane. This can be possibly accounted for by assuming that a methyl group in position 1 might shield all the three oxygen atoms, whereas methyl groups in positions 3, 7 and 10 shield only one atom each.

In summary, the results demonstrating the strong dependence of I on the spatial environment of oxygen atoms lead to the conclusion that the interaction between the oxygen atoms in silatrane rings and the acceptor groups of the stationary phase is one of the main factors responsible for the strong retention of silatranes. With silatranes this interaction is probably responsible for the total retention value to a greater extent than the orientational interaction between the molecules of silatranes and the stationary phase. Indirect evidence in favour of this assumption is provided by experiments with butylsilatranes used as the stationary phase. If orientational forces play a substantial role in the interaction of silatranes with the stationary phase, one would expect silatranes to possess equally high polarities when used as stationary phases and when used as solutes. On the other hand, if interaction of oxygen atoms with acceptor groups is essential, a high chromatographic polarity will occur only when a sufficiently large number of acceptor groups surround the silatrane molecule, in other words, if silatrane participates in the chromatographic process as a solute, but not as a stationary phase. However, if silatrane is the stationary phase, the chromatography of monofunctional polar substances would result in their interaction with only one of the three oxygen atoms. Measurements of McReynolds constants (benzene, 192; butanol, 344; methyl propyl ketone, 274; pyridine, 311; nitropropane, 443) demonstrated that when used as a stationary phase butylsilatrane exhibits only medium polarity. This also serves to support the assumption that the leading role in the interaction of silatranes with the stationary phase is played by the interaction between oxygen atom and the acceptor groups on the stationary phase rather than by the dipole moment of the molecule as a whole.

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