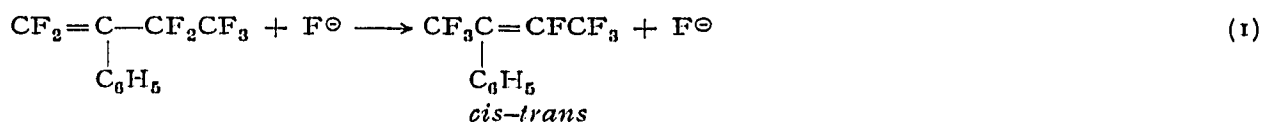


Gas chromatographic analysis of some isomeric phenyl-substituted perfluoro-olefins

In the course of an investigation¹ involving the fluoride ion catalyzed isomerization of terminal polyfluorinated olefins to mixtures of *cis* and *trans* internally substituted olefins (eqn. 1), it became necessary to separate and analyze isomeric



mixtures of the terminal, *cis*- and *trans*-perfluoro-olefins by gas-liquid chromatography (*cf.* Table I for physical properties of these olefins). The problem consisted primarily in the separation of the *cis* and *trans* isomers of 2-phenylheptafluoro-2-butene (compounds 1 and 3) and 2-phenylnonafluoro-2-pentene (compounds 4 and 5) respectively; and separation of a mixture consisting of the terminal 2-phenylheptafluoro-1-butene (compound 2) and the *cis* and *trans* isomers of 2-phenylheptafluoro-2-butene (1 and 3).

Although several columns gave some partial separation, silicone gum rubber, fluorosilicone rubber, Carbowax 20 M, and β,β' -oxydipropionitrile gave moderate to good separation of the *cis*- and *trans*-2-phenylheptafluoro-2-butene and 2-phenylnonafluoro-2-pentene isomers. However, only the use of β,β' -oxydipropionitrile (Fig. 1) and fluorosilicone rubber (Fig. 2) as liquid phases gave satisfactory separation of the three isomers of 2-phenylheptafluorobutenes (compounds 1, 2 and 3).

TABLE I
PHENYL SUBSTITUTED PERFLUORO-OLEFINS

$$\text{H}_5\text{C}_6 \begin{array}{l} \diagup \\ \diagdown \end{array} \text{C}=\text{C} \begin{array}{l} \diagdown \\ \diagup \end{array} \begin{array}{l} \text{B} \\ \text{C} \end{array}$$

Compound No.	A	B	C	B.p. °C (mm)	n_D^{20}
1	CF ₃	F	CF ₃	140-141 (740)	1.4049
2	C ₂ F ₅	F	F	138-139 (737)	1.4032
3	CF ₃	CF ₃	F	133-134 (740)	1.4004
4	CF ₃	C ₂ F ₅	F	145-146 (730)	1.3872
5	CF ₃	F	C ₂ F ₅	150-151 (739)	1.3918

Experimental and results

Carbowax 20 M (F & M Scientific) and fluorosilicone rubber (Dow Corning) were used to prepare 10% w/w packings on 100-120 mesh Gas Chrom P (Applied Science Lab.) and packed into a 10 ft. length of 1/4 in. O.D. copper tube and coiled. β,β' -Oxydipropionitrile (F & M Scientific) was used to prepare a 10% w/w packing on 80-100 mesh Chromosorb P (Applied Science Lab.) and packed into a 10 ft. length of 1/4 in. O.D. copper tube and coiled. Silicone gum rubber (F & M Scientific) was used to prepare a 10% w/w packing on 100-120 mesh Gas Chrom P and packed into a

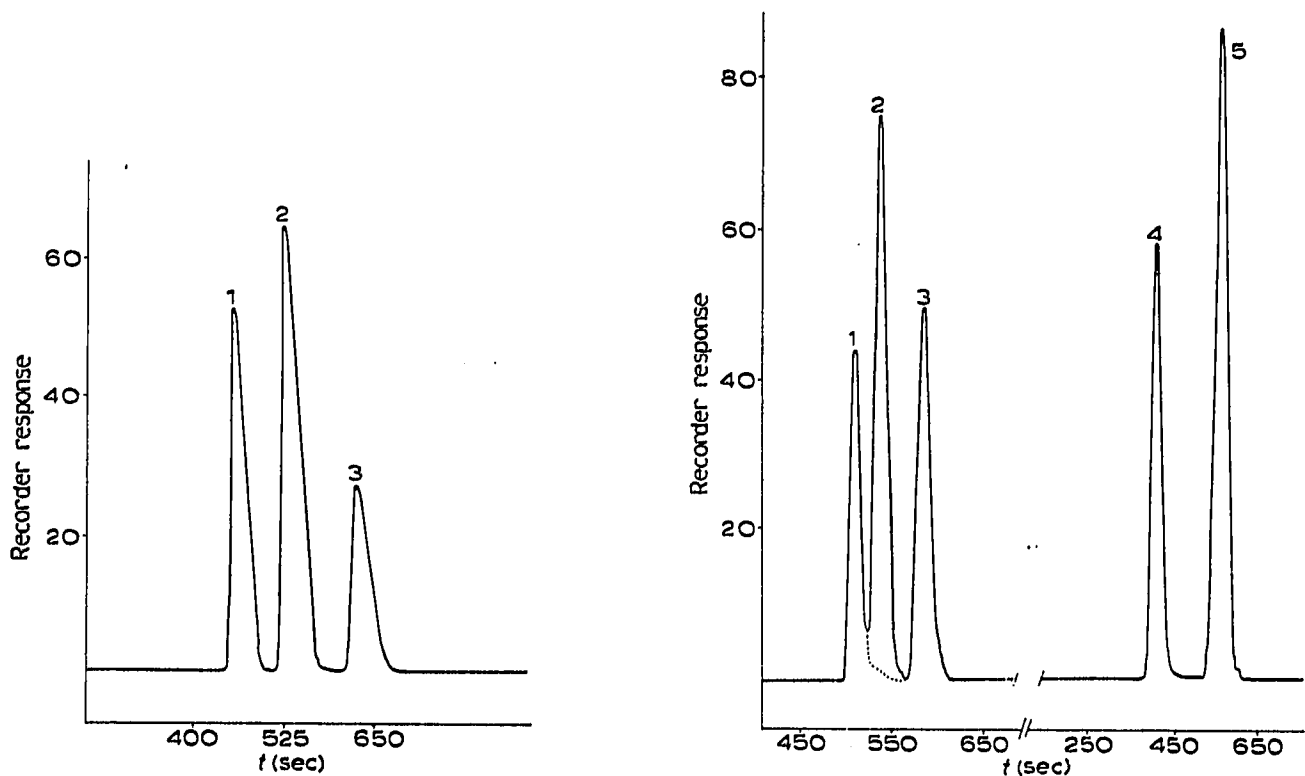


Fig. 1. Chromatogram of fluoro-olefins on β,β' -oxydipropionitrile. The numbers refer to those given in Table I.

Fig. 2. Chromatogram of fluoro-olefins on fluorosilicone rubber. The numbers refer to those given in Table I.

6 ft. length of $\frac{1}{4}$ in. O.D. copper tube and coiled. All chromatograms were obtained on an F & M Model 720 gas chromatograph with a helium flow rate of 60 ml/min with a pressure drop of 20 to 30 p.s.i. across the column. The sample size in all cases was 0.003 ml.

The results of the separations are given in terms of retention times (Table II) and the chromatograms of the fluoro-olefins are shown in Figs. 1 to 4. The dotted lines in Figs. 2, 3 and 4 indicate the separation of the *cis*- and *trans*-2-phenylhepta-

TABLE II

RETENTION TIMES OF FLUORO-OLEFINS

Packing	Temperature (°C)	Retention time (sec) of olefins				
		1	2	3	4	5
Silicone gum rubber	60	188	236	236	—	—
Silicone gum rubber	70	—	—	—	160	215
Fluorosilicone rubber	110	493	535	605	—	—
Fluorosilicone rubber	120	—	—	—	439	542
Carbowax 20 M	100	210	245	270	—	—
Carbowax 20 M	110	—	—	—	185	234
β,β' -Oxydipropionitrile	70	431	521	632	—	—

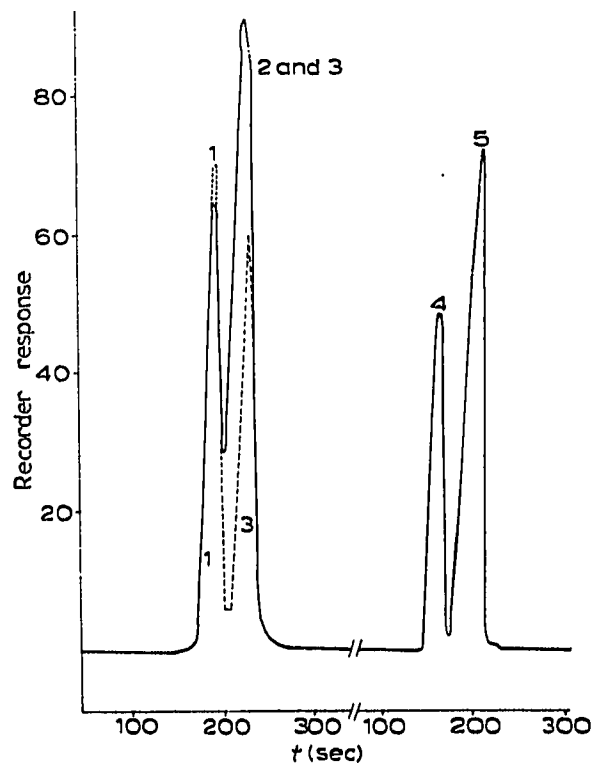
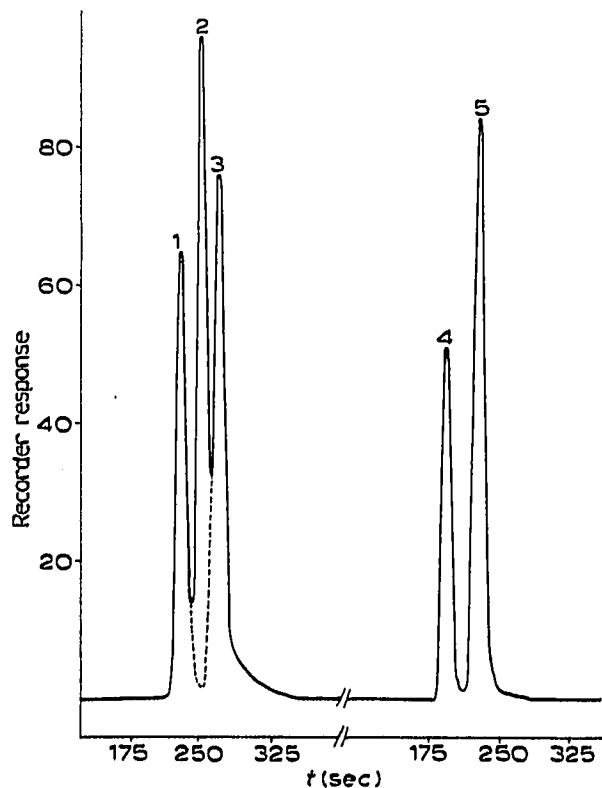


Fig. 3. Chromatogram of fluoro-olefins on Carbowax 20 M. The numbers refer to those given in Table I.

Fig. 4. Chromatogram of fluoro-olefins on silicone gum rubber. The numbers refer to those given in Table I.

fluoro-2-butene isomers on these columns, respectively, in the *absence* of the terminal olefin, 2-phenylheptafluoro-1-butene.

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1 D. J. BURTON AND F. E. HERKES, *Tetrahedron Letters*, (1965) 4509.

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