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EVALUATION OF SUBSTITUTED POLYPHENYL ETHERS AS POLAR PHASES IN GAS CHROMATOGRAPHY

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SUMMARY

Five- and six-ring *meta*-linked polyphenyl ethers containing NO₂, Br, CH₃CO, CH₂Cl and CN substituent groups have been prepared. The reaction conditions result in the formation of isomeric mixtures which can be analyzed by reversed-phase high-performance liquid chromatography. Although these substances are not suitable as starting materials for the synthesis of thermally stable reference stationary phases with a defined chemical structure, they do have useful stationary phase properties in their own right. The cyanopolyphenyl ethers (SPE-15 and SPE-16) have similar polarity to Carbowax 20M and Silar 5CP and are more thermally stable. They have good chromatographic properties and can be used to prepare high efficiency packed or capillary columns.

INTRODUCTION

The heart of any chromatographic system is the column. In gas-liquid chromatography, samples are separated by partition between a stationary liquid phase and a mobile gas phase. The influence of the carrier gas on the selectivity of the separation is minimal and the selection of the stationary phase is thus particularly important. Many liquids have been used as stationary phases¹. Most practitioners would say too many; and the expression "stationary phase pollution" has been coined to describe the substantial redundancy that exists in the market place for the sale of liquid phases of very similar separation characteristics and the proliferation of numerous brand names for the same product^{2,3}. Various authors, committees and societies have suggested that most chromatographic separations can be achieved on a limited number of "standard phases" – although there is no consensus in the literature as to how many such phases would be necessary^{4,5}.

A perusal of the stationary phase literature and suppliers catalogues indicates two deficiencies in currently available materials. There remains a need for selective

polar stationary phases which can be used at temperatures in excess of 300°C. Nearly all thermally stable stationary phases in use are polymeric substances which are characterized by an average molecular weight. As a consequence, they exhibit two undesirable features. They can not be reproduced exactly from batch to batch, and during column conditioning the lower molecular weight fraction is selectively evaporated from the column leaving behind an unknown weight of phase. Not wishing to pollute further the chromatographer's world, we have attempted to prepare thermally stable polar stationary phases having a defined chemical structure and absolute empirical formula. This effectively eliminates polymeric substances from consideration.

The polyphenyl ethers, originally synthesized by Ullman and Sponagel⁶, using the copper-catalyzed coupling reaction which now bears Ullman's name, have remarkably low volatility for their molecular weight. It was not until the 1950's that they were extensively evaluated as engine lubricants for operation in extreme environments and as diffusion pump fluids in mass spectrometers and high vacuum apparatus⁷. The *meta*-linked 5- and 6-ring phenoxy ethers (Fig. 1) are commercially available lubricants characterized by outstanding oxidation, radiation and thermal stability. They have been used as stationary phases in gas chromatography for the separation of a diverse range of compounds including aliphatic and aromatic hydrocarbons, steroids, carbohydrate derivatives and the neutral organic fraction from air particulate samples⁸⁻¹². Their McReynolds' constants, places them among the moderately polar stationary phases, and the *meta*-linked 5-ring phenoxy ether has an upper temperature operating limit of 200°C and the 6-ring ether of 250°C. A 20-ring phenoxy ether (in this case a true polymer as it contained an average of twenty rings) has been used¹³ as a stationary phase with an operating temperature range of 125-400°C.

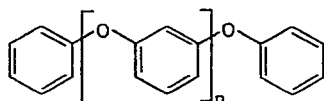


Fig. 1. Structure of the *meta*-linked polyphenyl ethers. $n = 3$ or 4.

The polyphenyl ethers have excellent thermal stability and chromatographic properties but lack the polarity to meet our original requirement. This situation could be changed by attaching to the polyphenyl ether backbone, side chains, selected to enhance the polarity/selectivity of the polyphenyl ethers without degrading their thermal stability.

Two broad strategies can be devised for the synthesis of the new phases. It should be possible to build up the polyphenyl ether chain by coupling together appropriately substituted phenoxy units with anchor groups to provide growth points for elaborating the polar side chain. Alternatively, the anchor groups could be introduced into the polyphenyl ether backbone by substitution reactions and then further modified as required. This latter route was investigated in this report as it involved "the minimum of synthesis" approach. For the anchor groups, Br, CH₃CO, CH₂Cl, CN and NO₂ were selected, as these can be introduced by direct reaction and are capable of further modification to other more reactive or selective side chains. These anchor groups are polar and selective in their own right and could lead to stationary phases with useful separation properties. The chemistry of the reactions used in this

study had not been established. Related reactions with biphenyl ether served as model systems for our study (reviewed in ref. 14).

EXPERIMENTAL

The 5-ring *meta*-linked polyphenyl ether (Santovac-5) and the 6-ring ether (OS-138) were obtained from Monsanto (St. Louis, MO, U.S.A.). Acetyl chloride, tin(IV) chloride, thallium acetate sesquihydrate and aluminum chloride were obtained from Aldrich (Milwaukee, WI, U.S.A.) and copper(I) cyanide from Alfa Products (Danvers, MA, U.S.A.).

General methods for preparing substituted polyphenyl ethers

Nitropolyphenyl ether (SPE-1). The 5-ring *meta*-linked polyphenyl ether (5.0 g) was stirred into 50 ml of an ice-cooled mixture of fuming nitric acid-sulfuric acid (7:3) and then maintained with stirring at room temperature for 3 h. The mixture was poured into ice and water and the red solid collected by filtration.

Nitropolyphenyl ether (SPE-2). The 5-ring *meta*-linked polyphenyl ether (5.0 g) was stirred into concentrated nitric acid (50 ml) and maintained at room temperature overnight. The mixture was poured into ice and water and the red solid collected by filtration (some oily material was discarded).

Nitropolyphenyl ether (SPE-5). The 5-ring *meta*-linked polyphenyl ether (6.8 g) was dissolved in acetic anhydride (40 ml) at 0°C and to this was added dropwise with stirring a solution of glacial acetic acid (30 ml) containing fuming nitric acid (2.0 ml) over a 2-h period. The mixture was stirred for a further 3 h at room temperature and then poured into ice and water. The oily residue was extracted with diethyl ether, washed with water, 10% sodium bicarbonate solution, water and dried over anhydrous sodium sulfate. The residue was dissolved in hexane containing a few percent of ethyl acetate and purified by silica gel column chromatography. The fractions eluted with 40 to 50% ethyl acetate in hexane were combined (this contained most of the polymer sample by weight) and the sticky yellow oil obtained was vacuum dried.

Acetylpolyphenyl ether (SPE-9). To the 5-ring *meta*-linked polyphenyl ether (10.0 g) in carbon disulfide (100 ml) was added in one portion aluminum chloride (10.0 g) and the mixture stirred for approximately 1 h under argon. To this was added acetyl chloride (6.0 ml) in one portion. An exothermic reaction occurred producing a green colored insoluble product. The mixture was heated to reflux for about 2 h, the solvent distilled off and the residue added to ice and water (vigorous reaction). The ethyl acetate extract was washed with water, 10% sodium bicarbonate, water and dried over anhydrous sodium sulfate. The residue was purified by silica gel chromatography, combining the fractions eluting with 40-60% ethyl acetate in hexane.

Chloromethylpolyphenyl ether (SPE-10). The 5-ring *meta*-linked polyphenyl ether (10.0 g) was dissolved in chloromethyl methyl ether (20 ml) in an ice-salt bath. To this was added slowly a solution of tin(IV) chloride (1.0 ml) in chloromethyl methyl ether (10.0 ml), the mixture refluxed for 3 h, cooled and the solid collected by filtration and vacuum dried. In the fume hood, the solid was powdered in a mortar and pestle, suspended in 10% (v/v) hydrochloric acid, filtered off and vacuum dried. The powdery white solid was only sparingly soluble in most common organic solvents.

TABLE I
PREPARATION AND PROPERTIES OF THE SUBSTITUTED POLYPHENYL ETHERS

Sample No.	Experimental conditions	No. of substituents	Empirical formula	m.p. (°C)
1 Nitro				
SPE-1	Fuming HNO ₃ -H ₂ SO ₄ (7:3)	8-9	C ₃₀ H _{14.3} N _{8.3} O _{23.2}	138-140
SPE-2	Conc. HNO ₃	3-4	C ₃₀ H _{19.4} N _{3.7} O _{12.2}	70-75
SPE-3	CH ₃ COOH-(CH ₃ CO) ₂ O-fuming HNO ₃ (3:4:1)	6	C ₃₀ H _{16.1} N ₆ O ₁₆	90-95
SPE-4	CH ₃ COOH-(CH ₃ CO) ₂ O-fuming HNO ₃ (10:13:1)	4	C ₃₀ H _{19.6} N _{4.1} O _{12.4}	75-85
SPE-5	CH ₃ COOH-(CH ₃ CO) ₂ O-fuming HNO ₃ (20:15:1)	2	C ₃₀ H _{21.2} N _{2.1} O _{8.2}	Liquid
SPE-6	CH ₃ COOH-(CH ₃ CO) ₂ O-fuming HNO ₃ (20:27:1)	1 to 2	C ₃₀ H _{20.3} N _{1.7} O _{7.7}	Liquid
SPE-7	CH ₃ COOH-(CH ₃ CO) ₂ O-fuming HNO ₃ (60:80:1)	1 to 2	C ₃₀ H _{20.6} N _{1.4} O _{6.7}	Liquid
SPE-8	CH ₃ COOH-(CH ₃ CO) ₂ O-fuming HNO ₃ (100:75:7)	3 to 4	C ₃₆ H _{27.7} N _{3.8} O _{13.6}	
2 Acetyl				
SPE-9	CH ₃ CO ₂ Cl/AlCl ₃	3		Liquid
3 Chloromethyl				
SPE-10	ClCH ₂ OCH ₃ /SnCl ₄	4	C ₃₄ H ₂₆ Cl ₄ O ₄ requires Cl = 22.19 found Cl = 22.11%	
4 Bromo				
SPE-11	Tl(OAc) ₃ /Br ₂	4	C ₃₀ H ₁₈ Br ₄ O ₄ requires Br = 41.99 found Br = 41.76	44-48
SPE-12		7	C ₃₀ H ₁₅ Br ₄ O ₇ requires Br = 56.06 found Br = 56.27	110-111
SPE-13		5	C ₃₆ H ₂₁ Br ₅ O ₅ requires Br = 42.87 found Br = 42.50	60-63
SPE-14		8	C ₃₆ H ₁₈ Br ₈ O ₅ requires Br = 54.70 found Br = 54.52	85-90
5 Cyano				
SPE-15	SPE-11/CuCN	3-4	C ₃₃ H _{20.8} Br _{0.67} N _{3.4} O ₄	65-70
SPE-16	SPE-13/CuCN	4-5	C _{40.3} H _{24.6} Br _{0.58} N _{4.6} O ₅	-

Bromopolyphenyl ether (SPE-11). To the 5-ring *meta*-linked polyphenyl ether (10 g) in carbon tetrachloride (100 ml) was added in one portion thallium acetate sesquihydrate (1.0 g) and the mixture stirred in the dark for 0.5 h. A carbon tetrachloride solution of bromine (3.6 g in 25 ml) was added dropwise with stirring over 1 h, the mixture heated to reflux for a further 1.5 h, cooled and the solvent removed on the rotavapor. The glassy solid was triturated with dioxane-hydrochloric acid-water (7:3:1), to remove the last traces of catalyst, and purified by silica gel chromatography. The bromopolyphenyl ether was eluted with dichloromethane and vacuum dried.

Bromopolyphenyl ether (SPE-14). To the 6-ring *meta*-linked polyphenyl ether (7.0 g) in carbon tetrachloride (50 ml) was added thallium acetate sesquihydrate (0.7 g) and the mixture stirred in the dark for 0.5 h. An excess of bromine (persistence of bromine color) was added dropwise and the solution stirred at room temperature for 1 h. The solution was heated to reflux for a further 6 h and portions of bromine added as required to maintain an excess in solution. The bromopolyphenyl ether was worked up as described for sample SPE-11.

Cyanopolyphenyl ether (SPE-15). The bromopolyphenyl ether (SPE-11, 10 g) was dissolved by heating to reflux in dimethylformamide, and to this was added in one portion copper(I) cyanide (17.0 g). The mixture was maintained at reflux for 7 h, cooled, poured into an aqueous solution of potassium cyanide (20 g in 200 ml) and filtered. The coarse solid was air dried and purified by silica gel chromatography. The cyanopolyphenyl ether was eluted with ethyl acetate-methanol (4:1) and vacuum dried.

Analysis and testing

The substituted polyphenyl ethers were analyzed by high-performance liquid chromatography (HPLC) using a Varian 5000 gradient-elution liquid chromatograph with a variable-wavelength UV-visible detector. The column was a 30 cm × 4 mm I.D. Micro-Pak CH-10, octadecylsilane reversed-phase column from Varian. For separation conditions see the figure legends.

For stationary phase testing a Varian 3700 or Varian 2000 gas chromatograph was used for both packed and capillary columns. Operating conditions are given in the figure legends.

Elemental analysis and thermal gravimetric analysis was provided by Spang Microanalytical Laboratory (Eagle Harbor, MI, U.S.A.).

RESULTS AND DISCUSSION

The elemental composition and physical properties of the substituted polyphenyl ethers are summarized in Table I. The thallic(III) acetate catalyzed bromination of the polyphenyl ethers is a facile reaction which can be used to control the number of bromine atoms introduced up to a certain maximum number (see SPE-12, SPE-14). However, not all these bromine atoms are as easily replaced as can be seen for the exchange reaction with cuprous cyanide (SPE-15, SPE-16). The exchange reaction between the bromopolyphenyl ether and *n*-butyllithium was not successful and did not provide a route to the carboxylic acid substituted compound. The introduction of the nitro group is not as specific as the introduction of bromine, but a

careful selection of the experimental conditions gives some control over the number of nitro groups introduced (SPE-3, SPE-4, SPE-5). Reduction of the nitro group to the amine occurs normally with a wide range of reducing agents. The acetyl (SPE-9) and chloromethyl (SPE-10) groups can be easily introduced into the polyphenyl ether backbone, but only in limited numbers. The chloromethyl substituted polyphenyl ether is unusual in being virtually insoluble in most common organic solvents and behaves atypically for a "benzyl chloride" derivative towards nucleophilic reagents. For example, with potassium cyanide, only approximately 62% of the available chlorine atoms can be substituted and with alkyl amines an even lower exchange was obtained. This low order of reactivity may simply be a reflection of its poor solvent solubility characteristics.

Elemental analysis provided an indication of the number of functional groups introduced but gave no information as to the position of introduction or the isomeric purity of the reaction product. Initial studies using nuclear magnetic resonance, gave complex results, not easy to interpret in the absence of standards, so an HPLC method was developed for their analysis. Fig. 2A illustrates that the commercially available 5-ring *meta*-linked polyphenyl ether is analytically pure and free from other oligomers. The controlled introduction of 4 bromine atoms into this (SPE-11) gives a minimum of 15 new peaks on HPLC analysis (Fig. 2B). Under forcing conditions, 7 bromine atoms are introduced and the chromatogram obtained much simplified

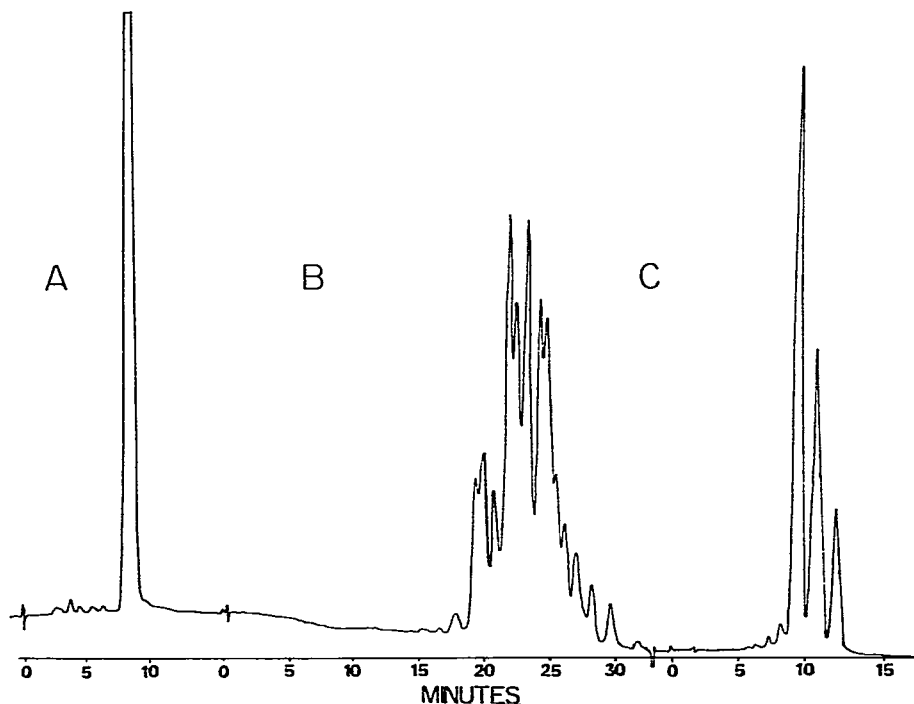


Fig. 2. HPLC separation of the 5-ring bromopolyphenyl ethers. A, Santovac-5, isocratic acetonitrile-water (17:3), flow-rate 1.0 ml min^{-1} , $\lambda = 240 \text{ nm}$. B, SPE-11, linear gradient acetonitrile-water, $T = 0$ (3:1) to $T = 30$ acetonitrile ($T =$ time in minutes), flow-rate 1.0 ml min^{-1} , $\lambda = 240 \text{ nm}$. C, SPE-12, linear gradient acetonitrile-water, $T = 0$ (19:1) to $T = 8$ acetonitrile, flow-rate 1.0 ml min^{-1} , $\lambda = 240 \text{ nm}$.

(SPE-12) (Fig. 2C). The thallium-catalyzed ring bromination would be expected to occur primarily in the *para* position to the phenoxy bond^{14,15}. For the 5-ring *meta*-linked polyphenyl ether, this would give 8 possible carbon centers for substitution. As there are more carbon centers than bromine atoms introduced, the complexity of the chromatograms is not surprising. In the limiting case (SPE-12) with 7 bromine atoms, there are 4 possible isomers, assuming that each carbon center is equally reactive towards the bromine reagent. Fig. 2C shows 3 main peaks (ratio 51:35:14) indicating an incomplete separation of the sample or preferred selective bromination of certain carbon centers resulting in an unequal isomer distribution. This latter assumption is supported by the fact that 7 and not 8 bromine atoms were introduced under forcing conditions and that not all the substituted bromine atoms are as easily replaced by reaction with cuprous cyanide. The situation with the 6-ring polyphenyl ether is more complex, as one would expect. Compare Fig. 3A which contains 5 bromine atoms (SPE-13) and Fig. 3B, the same polyphenyl ether containing 8 bromine atoms (SPE-14). Sample complexity diminishes as the number of bromine atoms is increased, but both chromatograms reflect the large number of possible isomers.

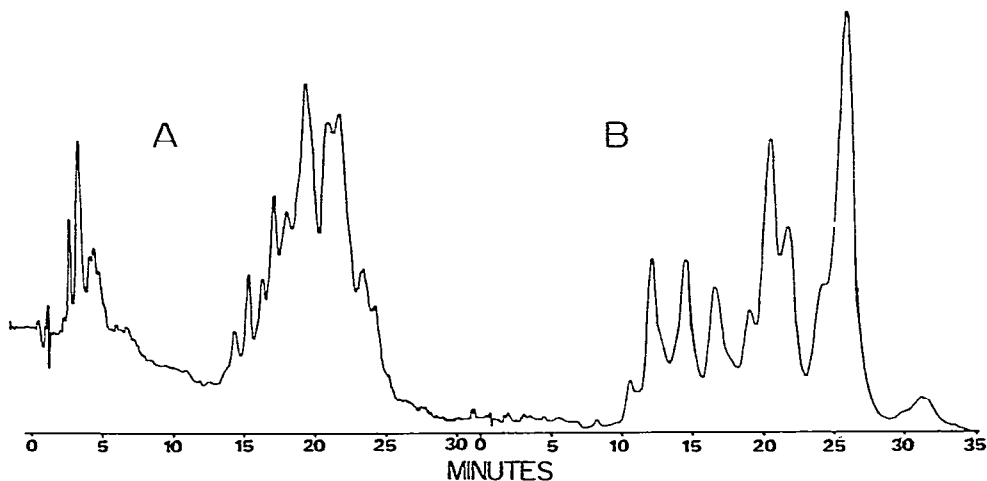


Fig. 3. HPLC separation of the 6-ring bromopolyphenyl ethers. A, SPE-13, linear gradient and flow program, acetonitrile-water, $T = 0$ (4:1), flow-rate 1.0 ml min^{-1} , $T = 8$ (21:4) isocratic, $T = 15$ (9:1), flow-rate 1.5 ml min^{-1} , $T = 27$ acetonitrile, $\lambda = 240 \text{ nm}$. B, SPE-14, isocratic and flow program, acetonitrile-water (91:9), $T = 0$ 1.0 ml min^{-1} , $T = 15$ 1.3 ml min^{-1} , $\lambda = 235 \text{ nm}$.

As eluded to previously, the reaction between cuprous cyanide and the bromopolyphenyl ethers containing 7 and 8 bromine atoms (SPE-12, SPE-14) does not go to completion. In the case of the 5-ring bromopolyphenyl ether containing 4 bromine atoms (SPE-11), nearly complete replacement is possible (SPE-15). However, the cyanopolyphenyl ether formed is a complex mixture of isomers (Fig. 4) reflecting the isomeric array of the starting material (SPE-11) and the fact that the sample contains a small percentage of residual bromine.

Direct nitration of phenyl ether results in substitution at C-2 and C-4 (ref. 14). C-4 substitution is much favored over C-2 and we hoped that reaction conditions with the polyphenyl ethers could be found to yield exclusively *para* substitution. The

TABLE II
CHROMATOGRAPHIC PROPERTIES OF THE SUBSTITUTED POLYPHENYL ETHERS

Sample No.	Type	Operating temperature (°C)		McReynolds' constants*										
		Minimum	Maximum	X	Y	Z	U	S	A	B	C	D	E	
	Five-ring polyphenyl ether	20	200	176	227	224	306	283	117	169	135	226	103	
	Six-ring polyphenyl ether	20	250	182	233	228	313	293	181	176	136	273	112	
SP-E-5	Nitropolyphenyl ether	50	220	236	344	356	398	194	259	255	182	409	210	
SP-E-9	Acetylpolyphenyl ether	50	200	244	390	312	449	394	299	253	164	365	-	
SP-E-11	Bromopolyphenyl ether	50	240	262	348	362	461	413	261	249	172	392	165	
SP-E-15	Cyanopolyphenyl ether	80	280	296	432	430	588	500						

* Test probes: X = benzene, Y = 1-butanol, Z = 2-pentanone, U = 1-nitropropane, S = pyridine, A = 2-methyl-2-pentanol, B = 1-iodobutane, C = 2-octyne, D = 1,4-dioxane and E = *cis*-hydrane.

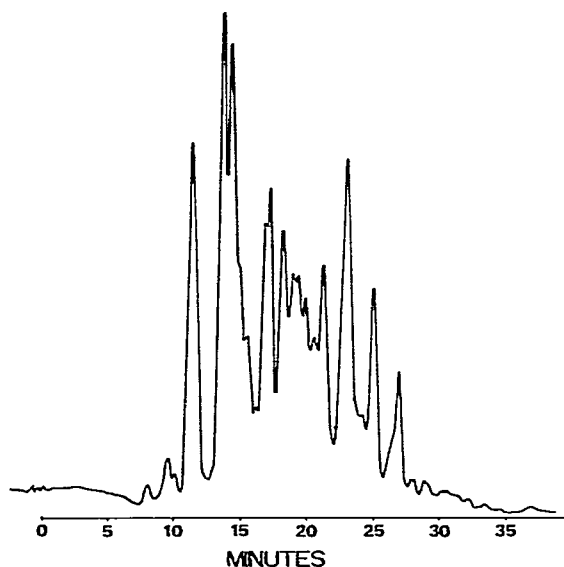


Fig. 4. HPLC separation of the cyanopolyphenyl ether SPE-15, linear gradient acetonitrile-water, $T = 0$ (3:2), $T = 40$ acetonitrile, flow-rate 1.0 ml min^{-1} , $\lambda = 245 \text{ nm}$.

most reactive conditions employed gave highly substituted derivatives (SPE-1 and SPE-2) but unfortunately these materials had poor storage properties and low thermal stability. The introduction of 6 nitro groups into the 5-ring polyphenyl ether (SPE-3) produced a more stable product with a simple isomer distribution (Fig. 5A).

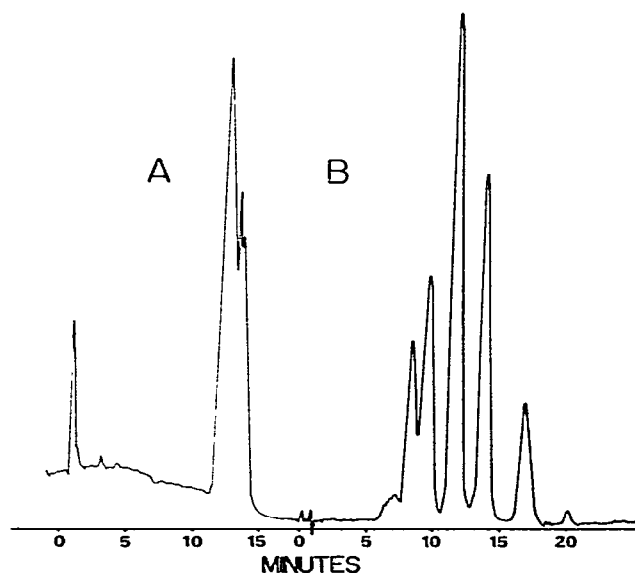


Fig. 5. HPLC separation of the nitropolyphenyl ethers. A, SPE-3, linear gradient, acetonitrile-water, $T = 0$ (3:2) to $T = 20$ acetonitrile, flow-rate 1.0 ml min^{-1} , $\lambda = 280 \text{ nm}$. B, SPE-5, isocratic, acetonitrile-water (3:1), flow-rate 1.0 ml min^{-1} , $\lambda = 300 \text{ nm}$.

If only two nitro groups are introduced (SPE-5), then the number of available reactive sites exceeds substantially the number of substituent groups and the isomer multiplicity is increased (Fig. 5B).

For reasons cited above, none of the materials prepared in this study meet our requirements as a starting point for a synthetically identified thermally stable polar stationary phase. They do have some useful chromatographic properties which are sufficiently encouraging to maintain our efforts to improve on the synthetic reactions described here. Table II summarizes the operating temperature range and McReynolds' constants for some of the substituted polyphenyl ethers we have prepared. The most polar of these phases (SPE-15) is somewhat similar in overall polarity to Carbowax 20M and Silar 5CP, but is more thermally stable than either. Compared to the polyphenyl ethers used as starting materials, the introduction of the substituent groups has increased the polarity and lowered the volatility of the stationary phases. Both features are desirable to meet our aim of preparing synthetically and structurally identified compounds of high polarity and thermal stability.

The stationary phases described in Table II had good chromatographic properties and we were able to prepare efficient packed and capillary columns with them. Fig. 6 shows a temperature-programmed separation of some normal aliphatic alcohols on a short packed column of SPE-15. Fig. 7 is a capillary column separation of a hydrocarbon mixture containing both pristane and phytane using SPE-16. Such mixtures originating from sedimentary rocks or archaebacteria are of some interest in

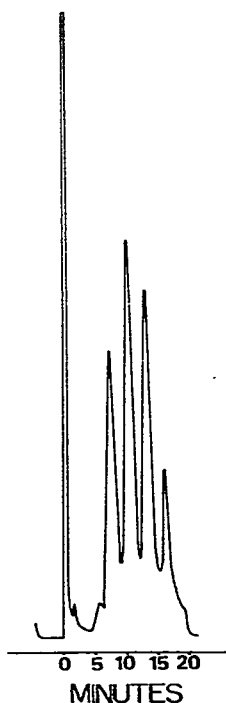


Fig. 6. Separation of the normal C_{12} to C_{15} aliphatic alcohols on a 0.5 m \times 4 mm I.D. glass column of 8% SPE-15 on Chromosorb W (80-100 mesh), nitrogen flow-rate 35 ml min^{-1} and temperature program 100 to 175°C at 4°C min^{-1} .

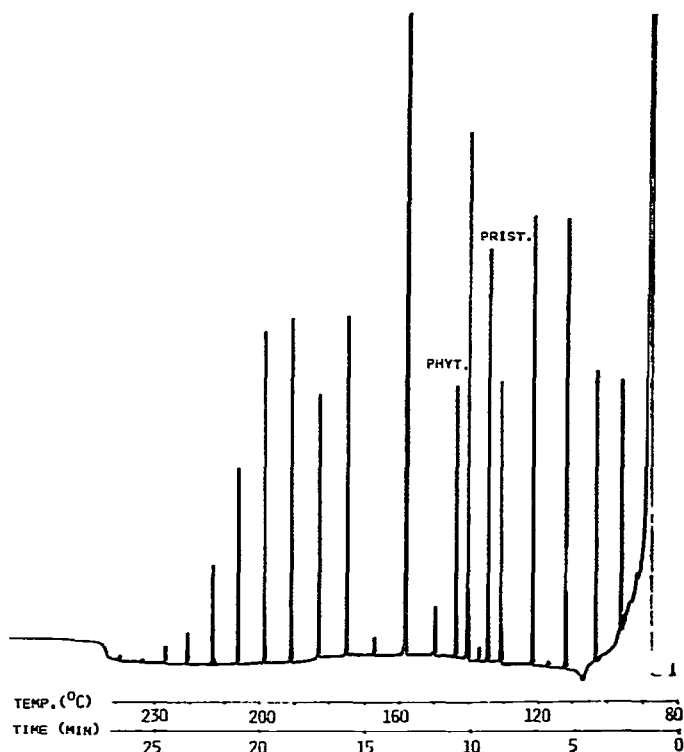


Fig. 7. Glass capillary column separation of the normal hydrocarbons C_{13} to C_{31} , pristane ($C_{19}H_{40}$, PRIST.) and phytane ($C_{20}H_{42}$, PHYT.). Column $15\text{ m} \times 0.35\text{ mm}$ I.D. wall-coated with SPE-16 and deactivated with Carbowax 20M treatment, helium flow-rate 3.0 ml min^{-1} , temperature program 80 to 230°C at 6°C min^{-1} , injector temperature 250°C .

the study of the biological processes which occurred on earth millions of years ago and for the discovery of new petroleum reserves¹⁶. The separation of pristane and phytane from their neighboring *n*-hydrocarbons on SPE-16 was better than we had previously obtained on any other capillary column including those coated with OV-101 which is normally used for this separation.

CONCLUSIONS

Substituted polyphenyl ethers with anchor polar groups capable of providing a site for the attachment of selected side chains can be prepared by simple reproducible reactions. These materials show useful separation properties as stationary phases in their own right and are more polar and more thermally stable than the parent polyphenyl ethers. The substitution reactions described lead to complex mixtures of isomers which are undesirable for the synthesis of a chemically defined thermally stable polar reference stationary phase. In the light of this finding, the synthesis of the necessary monomers suitably substituted with the anchor group and then coupling these together to give the desired product is likely to be the preferred route to these substances. This latter approach is currently under investigation.

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