Journal of Chromatography, 153 (1978) 181–188
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CHROM. 10,697

ALKYLATION OF PHENOL WITH C_8–C_{10} *n*-ALKENES

IDENTIFICATION AND GAS CHROMATOGRAPHIC BEHAVIOUR OF MONOALKYLPHENOLS

VITTORIO RAVERDINO and PIERGUIDO SASSETTI
Laboratorio Ricerche, Liquichimica Robassomero S.p.A., Robassomero (To.) (Italy)
(Received October 17th, 1977)

SUMMARY

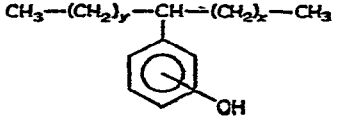
The analysis of monoalkylphenols obtained from the alkylation of phenol with C_8–C_{10} *n*-alkenes is described. Gas chromatography–mass spectrometry with different stationary phases for the capillary columns and the use of other analytical techniques allow the gas and liquid chromatographic behaviour of the isomers to be observed in environments of different polarity.

INTRODUCTION

Recent papers have reported the gas and liquid chromatographic behaviour of mono- and polyalkylphenols with relative short hydrocarbon chains using different coatings for the chromatographic columns[1–4].

In this work, the studies have been extended to monoalkylphenols in which the linear alkyl group contains 8–10 carbon atoms. These compounds, which are of interest mainly for the production of detergents and oil additives, are prepared by alkylation of phenol with *n*-alkenes, catalysed by acids and preferably by cationic resins. The position of the double bond influences the orientation of the substitution. However, the reaction can produce unexpected isomers as a result of a shift of the double bond along the hydrocarbon chain, thus changing the point of attachment of the ring. This behaviour has been observed even for α-alkenes. As pointed out by other workers for similar alkylation reactions, alkyl phenyl ethers can be formed to a certain extent[5].

n-Alkenes with an internal double bond usually react with phenol to produce all possible isomers. The series of products considered in this work are



(I)

with variable x and y and total carbon numbers of 14–16. 1-*n*-Octyl- and 1-*n*-nonylphenols have also been studied. Therefore, isomerization can be classified in two groups: "ring isomerism" (*ortho*-, *meta*- and *para*-) and "chain isomerism" (length of x and y chains).

EXPERIMENTAL

The compositions of the following samples were studied:

(a) C_{14} alkylphenols obtained by alkylation of phenol with α-octene.

(b) C_{15} alkylphenols from C_9 *n*-alkenes.

(c) C_{14}–C_{16} alkylphenols from industrial alkylation with C_8–C_{10} *n*-alkenes.

(d) 1-*n*-Octyl- and 1-*n*-nonylphenols (*ortho*- and *para*-isomers) synthesized by sulphonation of the correspondent 1-phenyl-*n*-alkane (Schuchardt, München, G.F.R.; "zur synthese") and alkaline fusion of the sulphonate[6]. These products were included as reference compounds for the analytical methods.

Each sample was previously derivatized in order to obtain convenient gas chromatographic separations and characteristic mass spectra for the identification of the ring and chain isomers[1]. Acetylation was found to be adequate in both respects.

Gas chromatograms were obtained with a Carlo Erba GI gas chromatograph and a flame-ionization detector. Gas chromatographic–mass spectrometric (GC–MS) analyses were performed by coupling a Varian 2700 gas chromatograph with a Varian CH5 mass spectrometer equipped with a single-stage Biemann–Watson separator[7] and an electron-impact ion source operating at an ionization potential of 18 eV at a temperature of 250°. Capillary columns coated with DC 550 (phenylmethylsilicone oil; 100 m × 0.25 mm I.D.), GAL (Apiezon grease; 50 m × 0.25 mm I.D.) and Carbowax 20M (polyethylene glycol; 25 m × 0.25 mm I.D.) were used. Some of the GC and MS data were supplemented by results obtained by other analytical techniques: high-performance liquid chromatography (HPLC) for the separation of *ortho*-, *meta*- and *para*-isomers and infrared spectrophotometry for the identification of the isolated fractions. A Waters Assoc. ALC–GPC 201 high-pressure liquid chromatograph equipped with a double pumping system and a Perkin-Elmer LC-55 UV detector, and a Perkin-Elmer 377 infrared spectrophotometer were used for these determinations.

RESULTS AND DISCUSSION

Gas chromatographic behaviour

Gas chromatograms of samples (a), (b) and (c) (see Experimental) are shown in Fig. 1. The order of elution of the isomers for the C_{14}–C_{16} mixture is given in Table I.

Peaks not listed in Table I represent small amounts of branched-chain isomers and alkyl phenyl ethers with low retention times. The *m*-C_{16} derivative could not be detected.

Retention times of the isomers identified are given in Table II.

The typical gas chromatographic behaviour of these compounds can be summarized as follows:

(1) The retention times of the isomers increase in the sequence *ortho*-, *meta*- and *para*-. *Meta*-isomers overlap partially with the *ortho*- and *para*-isomers of the

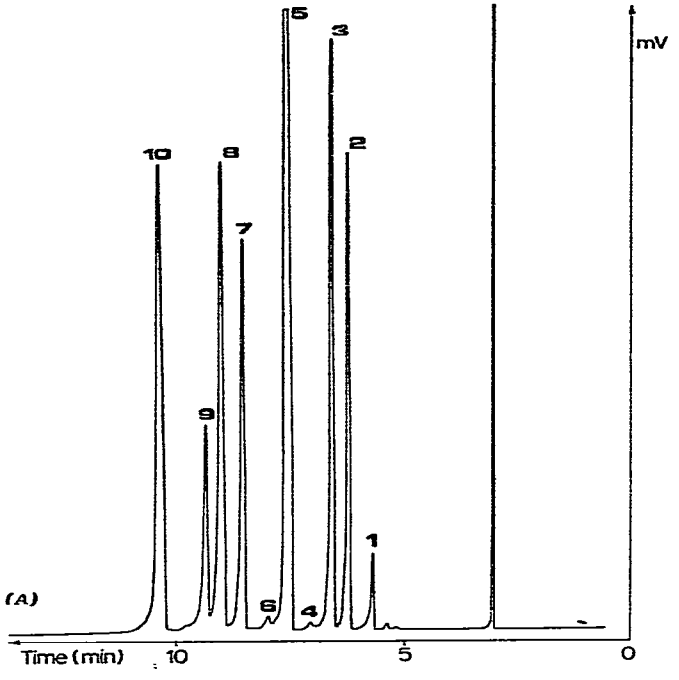


Fig. 1 (a)

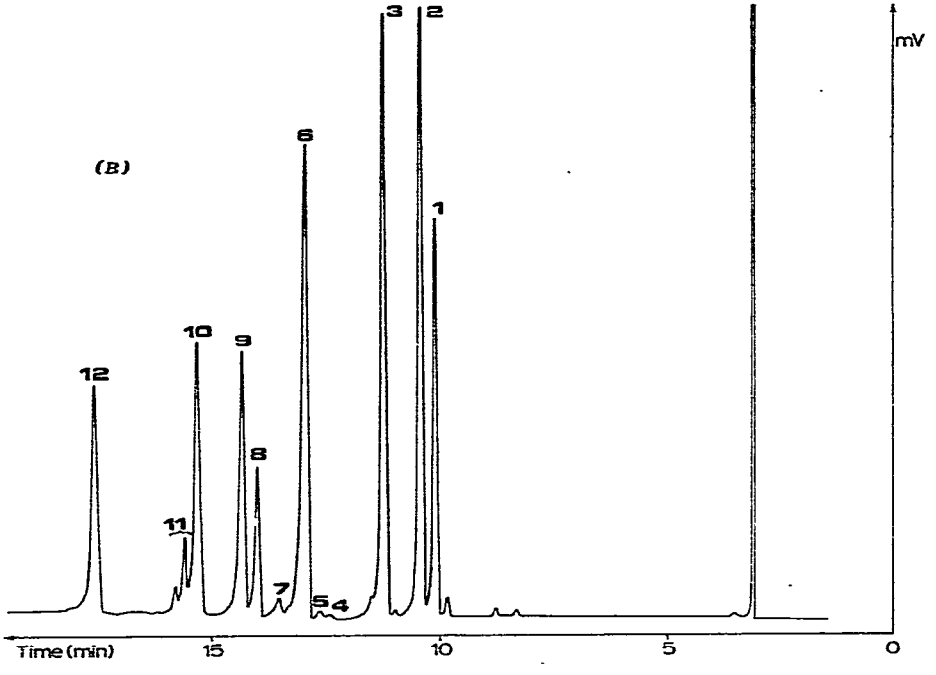


Fig. 1 (b)

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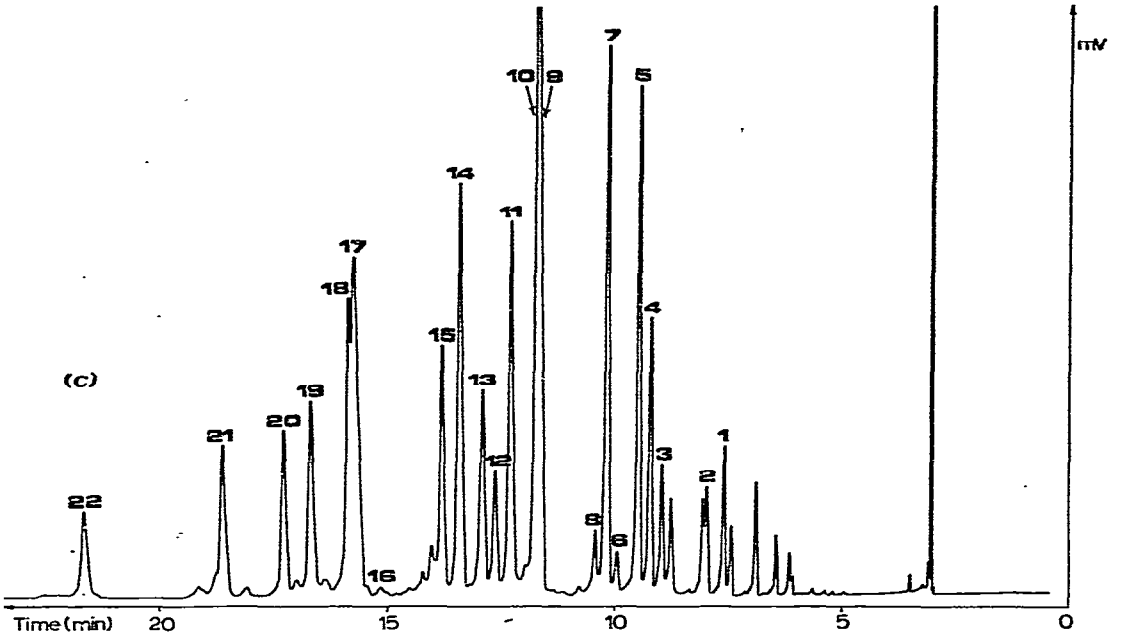


Fig. 1. Gas chromatograms of acetylated monoalkylphenols from alkylation of phenol with (a) α-octene, (b) *n*-nonene and (c) a mixture of C_8–C_{10} *n*-alkenes. *Meta*-isomers are present in low concentration. Column (100 m × 0.25 mm I.D.) coated with DC 550. Peaks in chromatogram (a): 1 = octyl phenyl ether; 2 = *o*-4-pH-octane; 3 = *o*-3-pH-octane; 4 = *m*-4-pH-octane; 5 = *o*-2-pH-octane; 6 = *m*-3-pH-octane; 7 = *p*-4-pH-octane; 8 = *p*-3-pH-octane; 9 = branched-chain isomers; 10 = *p*-2-pH-octane. Peaks in chromatogram (b): 1 = *o*-5-pH-nonane; 2 = *o*-4-pH-nonane; 3 = *o*-3-pH-nonane; 4 = *m*-5-pH-nonane; 5 = *m*-4-pH-nonane; 6 = *o*-2-pH-nonane; 7 = *m*-3-pH-nonane; 8 = *p*-5-pH-nonane; 9 = *p*-4-pH-nonane; 10 = *p*-3-pH-nonane; 11 = branched-chain isomers + *m*-2-pH-nonane; 12 = *p*-2-pH-nonane. Peaks in chromatogram (c) are identified in Table I.

TABLE I

ORDER OF ELUTION OF THE C_{14}–C_{16} ACETYLATED MONOALKYLPHENOL MIXTURE

Peak numbers are related to gas chromatogram (c) in Fig. 1. The acetylated phenol group is indicated by "-pH-".

Compound	*Peak No.*	*Compound*	*Peak No.*
o-4-pH-octane	1	*p*-2-pH-octane	10
o-3-pH-octane	2	*o*-2-pH-nonane	
m-4-pH-octane		*m*-3-pH-nonane	
o-2-pH-octane	3	*o*-4-pH-decane	11
o-5-pH-nonane	4	*p*-5-pH-nonane	12
o-4-pH-nonane	5	*p*-4-pH-nonane	13
m-3-pH-octane		*o*-3-pH-decane	14
p-4-pH-octane	6	*p*-3-pH-nonane	15
m-2-pH-octane		*o*-6-pH-undecane	16
o-3-pH-nonane	7	*o*-2-pH-decane	17
m-5-pH-nonane		*p*-2-pH-nonane	18
m-4-pH-nonane		*p*-5-pH-decane	19
p-3-pH-octane	8	*p*-4-pH-decane	20
o-5-pH-decane	9	*p*-3-pH-decane	21
		p-2-pH-decane	22

TABLE II

GAS CHROMATOGRAPHIC RETENTION TIMES OF ACETYLATED MONOALKYLPHENOLS

Column (100 m × 0.25 mm I.D.) coated with DC 550. Temperature, 185°; flow-rate, 1 ml/min. Retention times are expressed in arbitrary units. N.D. = not determined. The acetylated phenol group is indicated by "-pH-".

Alkyl chain	*Compound*	*Ortho*	*Meta*	*Para*
C_8	1-*n*-Octylphenol	138	168	193
	2-pH-octane	96	N.D.	141.5
	3-pH-octane	80.5	104	120
	4-pH-octane	74	83	112
C_9	1-*n*-Nonylphenol	210	N.D.	290
	2-pH-nonane	141.5	N.D.	209.5
	3-pH-nonane	116	147	175.5
	4-pH-nonane	105	134	161
	5-pH-nonane	100.5	131.5	156
C_{10}	2-pH-decane	207	N.D.	302
	3-pH-decane	169	N.D.	253.5
	4-pH-decane	151	N.D.	232
	5-pH-decane	141.5	N.D.	222.5

same carbon number while only the acetylated *o*-1-*n*-alkylphenols appear near the *para*-isomers.

(2) It has been observed that when a very polar stationary phase (Carbowax 20M) is used (Fig. 2), structural differences in ring isomerism are not particularly noticeable.

However, isomers with the same ring isomerism and carbon number tend to cluster as the polarity increases. As shown in Table III, this effect is more pronounced for the *para*-isomers; retention times are referred to the 2-pH-nonane with the same ring isomerism (R values) in order to demonstrate how much the "internal" isomers are clustered with the "external" isomers. In the cases examined, it appears that increasing the polarity of the partition liquid (GAL, DC 550, Carbowax 20M) increases the R values of the "internal" isomers, especially the *para*-isomers.

(3) Additional data on this aspect were been obtained by HPLC using a polar support for the chromatographic separations (μPorasil). As shown in Fig. 3, the most "internal" non-acetylated alkylphenols with same ring isomerism have lower retention times. The acetyl derivatives could be separated only as groups, the separation of *ortho*- and *para*-isomers under similar conditions being poor. It should be pointed out that the HPLC separations of the *para*- and *meta*-isomers were more difficult than that of the *ortho*-isomers. As shown in Fig. 3, the three positional isomers of *o*-octylphenol are well separated, while the *para*- and *meta*-isomers cannot be completely resolved, even on changing solvent concentrations. If correct, this result could be related to the chain *para*-isomer clustering mentioned above.

Mass spectra of the acetylated alkylphenols (I)

As shown below, isomer identifications can be performed by observing the

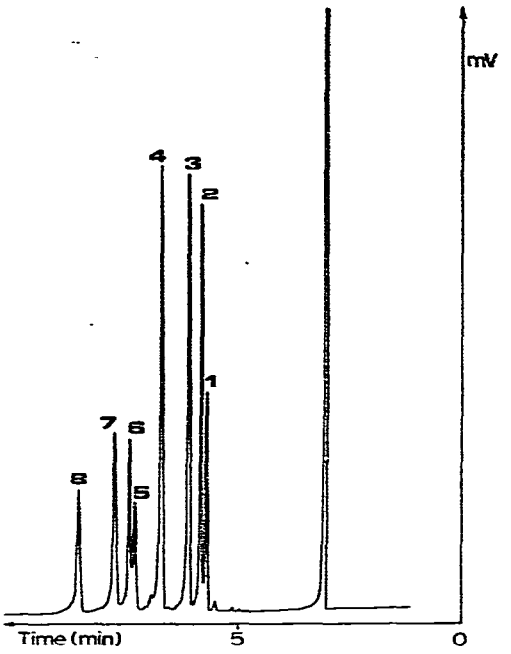


Fig. 2. Gas chromatogram of acetylated nonylphenols obtained on a steel capillary column (25 m × 0.25 mm I.D.) coated with Carbowax 20M. Temperature, 175°; nitrogen flow-rate, 1 ml/min. Peaks: 1 = *o*-5-pH-nonane; 2 = *o*-4-pH-nonane; 3 = *o*-3-pH-nonane; 4 = *o*-2-pH-nonane; 5 = *p*-5-pH-nonane; 6 = *p*-4-pH-nonane; 7 = *p*-3-pH-nonane; 8 = *p*-2-pH-nonane.

TABLE III

COMPARISON BETWEEN GAS CHROMATOGRAPHIC RELATIVE RETENTION TIMES OF ACETYLATE NONYLPHENOLS USING DIFFERENT STATIONARY PHASES

Figures in the "Position" column indicate the point of ring substitution on the alkyl chain: 2 = acetyl-2-pH-nonane, 3 = acetyl-3-pH-nonane, etc. *R* values indicate the ratios between the net retention times of the internal positional isomers and of the 2-positional isomers.

Stationary phase	*Position*	R_{ortho}	R_{para}
GAL	2	1	1
	3	0.80	0.83
	4	0.71	0.74
	5	0.68	0.71
DC 550	2	1	1
	3	0.82	0.84
	4	0.74	0.76
	5	0.71	0.74
Carbowax 20M	2	1	1
	3	0.84	0.85
	4	0.76	0.81
	5	0.73	0.78

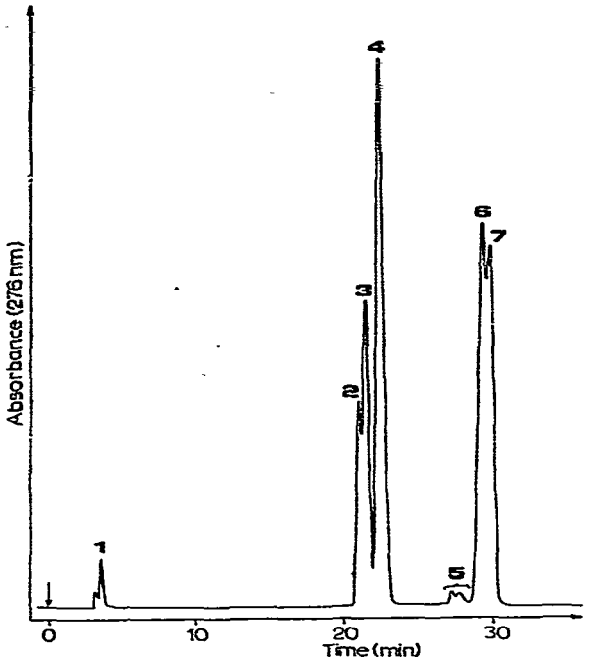
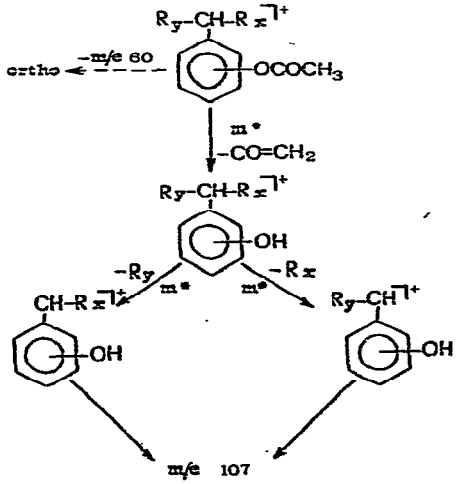


Fig. 3. HPLC of octylphenols. Column: 300 × 4 mm I.D. packed with μPorasil, 10 μm average particle size. Solvent programme: concave programme enriched with isoctane, from 2% to 30% chloroform in isoctane in 20 min. Flow-rates 1.2 ml/min. Δp = 550 p.s.i. Room temperature. UV Detector operating at 276 nm. Peaks: 1 = octylphenyl ether; 2 = *o*-4-pHOH-octane; 3 = *o*-3-pHOH-octane; 4 = *o*-2-pHOH-octane; 5 = *meta*-isomers; 6 = mixture of *p*-4 and *p*-3-pHOH-octane; 7 = *p*-2-pHOH-octane. pHOH = not acetylated phenol ring.

specific fragmentations of the alkyl groups from the point of substitution of the hydrocarbon chain:



This type of fragmentation is characteristic of the alkyl-benzenes and of other compounds of similar structure[8–10]. As expected, methyl fragmentation is less favoured

when R_x or $R_y = CH_3$. The *ortho*-effect leads to the formation of a weak peak by a total loss of $C_2H_4O_2$ from the molecular ion. *Meta*- and *para*-isomers cannot be distinguished from the mass spectra and MS identifications have therefore to be confirmed by other analytical techniques (HPLC and IR spectrophotometry for the separation and identification of the separated fractions).

Alkyl phenyl ether impurities found at the beginning of the GC and HPLC chromatograms gave an intense characteristic peak at *m/e* 94 in the mass spectra.

CONCLUSIONS

Monoalkylphenols obtained by alkylation of phenol with C_8–C_{10} *n*-alkenes have been analyzed by GC–MS and other techniques. Components that differ in both "ring isomerism" (*ortho*-, *meta*- and *para*-) and "chain isomerism" (position of the ring on the hydrocarbon chain) have been separated and identified. The order of increasing elution times is generally *ortho*-, *meta*- and *para*. This behaviour is followed even in the HPLC of the acetylated and non-acetylated products using a polar support (μPorasil), and the elution times are lower for the isomers in which the ring is substituted in the positions nearest to the centre of the hydrocarbon chain.

The use of stationary phases of different polarity in the GC capillary columns revealed a certain tendency of the chain isomers with same ring isomerism and the same carbon number to cluster as the polarity increases. This effect is particularly striking for the *para*-isomers.

Similar behaviour seems to occur in the HPLC of the alkylphenol mixture, the *para*-isomers being resolved hardly more than the correspondent *ortho*-isomers when a very polar support is used. However, it must be pointed out that the approach considered does not take into account important aspects of the solid–liquid–vapour equilibria.

ACKNOWLEDGEMENT

We thank Mr. R. Ghelli and Mr. A. Cannizzo for their technical and analytical contributions.

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