

Esters of isomeric arylundecanoic acids

N. F. EWEISS

Department of Chemistry, University of Kuwait

ABSTRACT

Methyl undecenoate and undecenyl alcohol were condensed with different alkyl- and halobenzenes using a Lewis acid. The condensation products, a mixture of aryl-substituted esters or alcohols, were oxidised by chromic acid. The resulting alkyl aryl ketones were analysed by gas-liquid chromatography and were found to be a mixture of six isomers with the aryl group on carbon five to carbon ten of the paraffinic chain.

INTRODUCTION

The reaction of methyl undecenoate with benzene and toluene using anhydrous aluminium chloride was previously investigated. The distilled reaction product was analysed by gas-liquid and thin-layer chromatography (Achaya & Amma 1967) and found to be a mixture of three isomeric methyl arylundecanoates, i.e. the 10-(39%), 9-(17%), and 8-(44%) aryl isomers. However, five peaks were obtained in the analysis of the distilled product by capillary chromatography and mass spectrometry (Zeman *et al.* 1969), one of which corresponded to the 5- and 6-aryl isomers together (11.6%). The other four peaks represented the 7-(15.1%), 8-(17.0%), 9-(21.0%), and 10-(35.3%) aryl isomers.

In the present study we wish to report that the gas-liquid chromatography of the mixture of ketones obtained by chromic acid oxidation of methyl arylundecanoate and arylundecanol revealed six position isomers with substitution at carbon five to carbon ten for both the ester and the alcohol. A higher percentage of the 5-aryl isomer is observed in the case of the alcohol than in the ester. It seems worth mentioning that the percentage of the 5-aryl and 6-aryl isomers was determined separately, which was not possible by capillary chromatography (Zeman *et al.* 1969). Besides, the distribution of the isomeric methyl arylundecanoate and arylundecanol was also investigated.

RESULTS AND DISCUSSION

Methyl arylundecanoate and phenylundecanol were chromatographed using Pye Argon chromatograph (4 ft column with 10% Apiezon L or 10% polyethylene glycol adipate on celite 100–120 mesh). The alkyl aryl ketones resulting from oxidation of the methyl arylundecanoate and phenylundecanol were chromatographed using either the

above mentioned chromatograph or the Hewlett Packard Research dual column temperature-programmed gas chromatograph Model 5751 (8 ft stainless steel column containing 25% silicon grease on celite 60–100 mesh).

Gas-liquid chromatography of the distilled methyl arylundecanoate and phenylundecanol revealed that neither of them is a single component. The number of peaks with the percentage of the corresponding components are shown in Table 1 and Figs 1 and 2. Direct identification of these different peaks that represent the different isomers resulting from either double bond isomerisation or *o*- and *p*-substitution was not possible. However, chromic acid oxidation of the methyl arylundecanoates and phenylundecanol followed by gas chromatography of the degradation products was applied to determine the structure of the isomers. Thus, oxidation of methyl phenylundecanoate yielded a mixture of six alkyl aryl ketones. These were identified and compared with authentic samples (see experimental part), and their percentage

Table 1. Gas-liquid chromatography* of methyl arylundecanoates and phenylundecanol

Peak	Methyl arylundecanoate					phenylundecanol (%)
	phenyl (%)	<i>p</i> -tolyl (%)	<i>p</i> -anisyl (%)	<i>p</i> -chlorophenyl (%)	<i>m</i> -xylyl (%)	
1	27.8	33.2	9.1	34.3	46.0	17.8
2	14.2	20.2	7.1	23.2	14.1	21.4
3	17.3	16.5	17.7	19.6	20.4	22.2
4	40.7	4.6	47.4	5.5	19.5	38.6
5		17.4	8.0	12.7		
6		8.1	10.7	4.7		

* Using Pye Argon chromatograph (4 ft column with 10% Apiezon L or 10% polyethylene glycol adipate on celite 100–120 mesh).

determined. They proved to be: acetophenone (41.6%), propiophenone (13.6%), butyrophenone (14.3%), valerophenone (15.9%), caprylophenone (12.2%), and heptophenone (2.4%). These ketones would arise from the oxidation of the methyl phenylundecanoate isomers with the phenyl group in positions 10-, 9-, 8-, 7-, 6-, and 5-, respectively. This shows that through the oxidation step it was then possible to determine the percentage of the 6-phenyl and 5-phenyl isomers separately. Other methyl arylundecanoates were treated similarly and the distribution of their isomers, determined by gas-liquid chromatography of the product of their oxidation with chromic acid, is reported in Table 2.

Smith *et al.* (1965) reported the preparation of methyl phenylstearate from methyl oleate and showed that the attachment of the phenyl group in the isomers would not progress further than carbon six. They attributed this to the possible formation of a δ -lactone from the intermediate carbocation, thus preventing it from further isomerisation. Since the presence of methyl 5-phenyl- and 5-*p*-tolylundecanoate has been proved in this report, then the formation of a stable γ -lactone cannot be ignored. It is significant to point out that Placek & Bickford (1961) working on the hydroxylation of oleic acid showed that, through isomerisation, the attachment of the

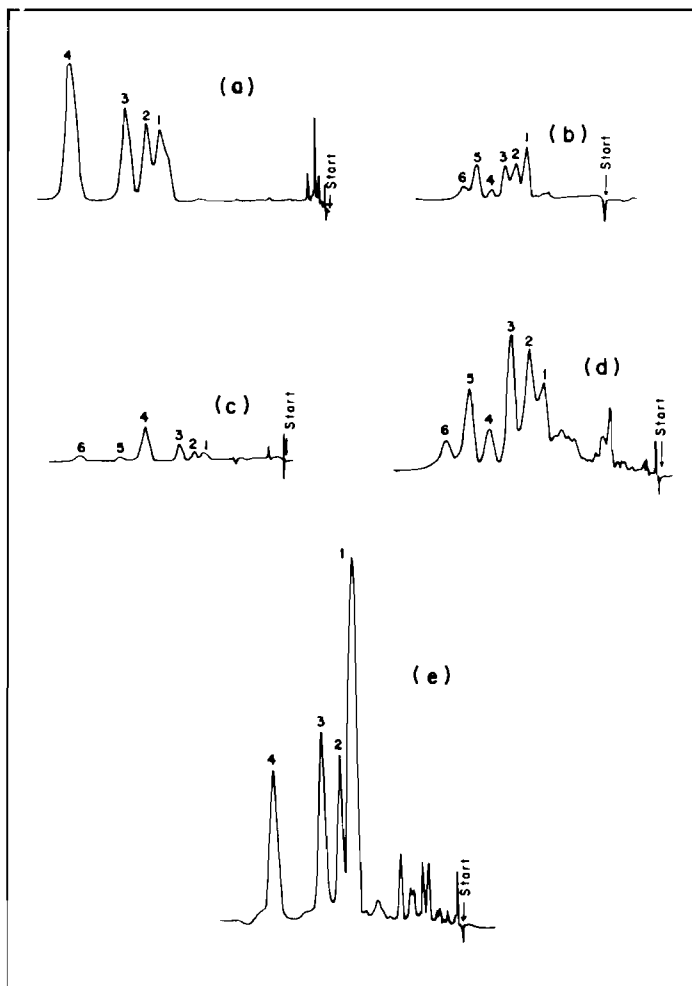


Fig. 1. Gas-liquid chromatography of methyl arylundecanoate (a) phenyl, (b) *p*-tolyl, (c) *p*-anisyl, (d) *p*-chlorophenyl, (e) *m*-xylyl. [Using Pye Argon chromatograph (4 ft column with 10% Apiezon L or 10% polyethylene glycol adipate on celite 100–120 mesh)].

hydroxyl group wanders till carbon five. This finding is also supported by the work of Zeman *et al.* (1969).

In addition Table 2 shows the isomeric distribution of phenylundecanol, prepared by the phenylation of undecenyl alcohol, as revealed by gas-liquid chromatography of the ketones obtained by chromic acid oxidation of the product. It is clear that in the phenylation of undecenyl alcohol, compared with the phenylation of methylundecenoate, a higher percentage of the 5-aryl isomer was obtained. This could be attributed to the fact that lactone formation in the former case is not possible.

EXPERIMENTAL

Fractional distillation *in vacuo* was carried out using Edwards speedivac high vacuum

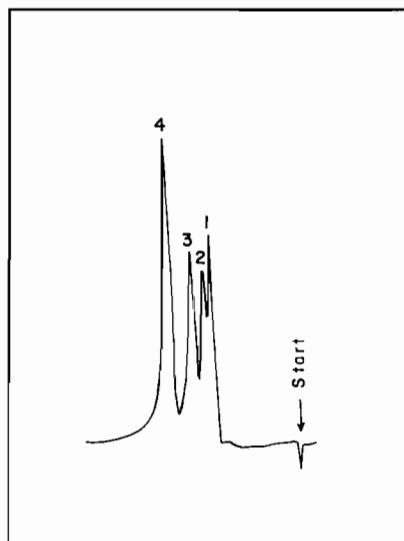


Fig. 2. Gas-liquid chromatography of phenylundecanol. [Using Pye Argon chromatograph (4 ft column with 10% Apiezon L or 10% polyethylene glycol adipate on celite 100–120 mesh)].

Table 2. Distribution*,† of isomeric methyl arylundecanoate and phenylundecanol

Position of aryl group	Methyl arylundecanoate					phenylundecanol (%)
	phenyl (%)	<i>p</i> -tolyl (%)	<i>p</i> -anisyl (%)	<i>p</i> -chlorophenyl (%)	<i>m</i> -xylyl (%)	
C ₁₀	41.6	20.2	47.6	53.2	45.7	41.5
C ₉	13.6	4.5	25.9	7.1	10.6	7.3
C ₈	14.3	6.7	17.1	8.3	10.4	6.4
C ₇	15.9	15.4	6.1	18.9	14.1	12.7
C ₆	12.2	19.0	3.3	12.5	19.2	12.8
C ₅	2.4	34.2				19.3

* Based on the structure of the products obtained after oxidation with chromic acid.

† Determined by gas-liquid chromatography using Pye Argon chromatograph (4 ft column with 10% Apiezon L or 10% polyethyleneglycol adipate on celite 100–120 mesh) or Hewlett Packard Research dual column temperature-programmed gas chromatograph Model 5751 (8 ft stainless steel column containing 25% silicon grease on celite 60–100 mesh).

pump Model ES200. Refractive indices were determined by A0 Abbe refractometer Model 10460. The determination of iodine values, saponification equivalents and alcoholic hydroxyl group, and the preparation of 2,4-dinitrophenylhydrazones of the investigated alkyl aryl ketones was carried out according to standard procedures (Pasto & Johnson 1969).

Undecenoic acid and its methyl ester

The acid was prepared according to the procedure reported by Subbarao & Achaya (1962). The crude acid was distilled and the fraction boiling at 141–142°C/1.5 mm was collected, esterified with methanol and then fractionally distilled to give methyl undecenoate, b.p. 93°C/0.8 mm ($n_D^{27} = 1.45852$; iodine value = 127.6; saponification equivalent = 198.0).

Methyl arylundecanoate

Methyl undecenoate (0.15 mole) was added dropwise during 1 hr to a stirred suspension of anhydrous aluminium chloride (0.17 mole) in the appropriate aromatic substrate (0.8 mole). This procedure is similar to the preparation of isomeric phenylstearic acids (Smith *et al.* 1968). The products were fractionally distilled *in vacuo* and their characteristics are summarised in Table 3.

Table 3. Methyl arylundecanoate

Aryl group	B.p. (°C/mm)	n_D^{27}	Molecular weight	
			Saponification equivalent	Calculated
phenyl	123–129/0.5	1.48426	275.00	276
<i>p</i> -tolyl	132–141/0.6	1.49438	291.00	290
<i>p</i> -anisyl	148–153/0.5	1.49062	308.20	306
<i>p</i> -chlorophenyl	162–176/0.6	1.49926	306.00	310
<i>m</i> -xylyl	133–140/0.6	1.48862	308.60	304

Undecenyl alcohol

Methyl undecenoate was reduced with lithium aluminium hydride according to the procedure given by McCutcheon *et al.* (1959). The product was distilled to give undecenyl alcohol, b.p. 84–89°C/1 mm: $n_D^{27} = 1.44973$; iodine value, 148.0; alcoholic hydroxyl, 9.89%.

Phenylundecanols

The mixture of isomeric phenylundecanols was prepared by phenylation of undecenyl alcohol in excess of benzene using anhydrous aluminium chloride. The product was distilled to give the phenylundecanols, b.p. 143–149°C/0.5 mm, iodine value, nil; alcoholic hydroxyl, 6.83%.

The lithium aluminium hydride reduction of the mixture of methyl phenylundecanoate gave a mixture of isomeric phenylundecanols that proved to be identical in every respect with the mixture prepared earlier.

Chromic acid oxidation

The oxidation was carried out as reported by Smith *et al.* (1965 & 1967), where methyl

arylundecanoate (0.1 mole) and chromic acid (0.6 moles) were heated in glacial acetic acid (1 mole) for 1 hr. In case of phenylundecanols, the ratio of chromic acid was increased to seven folds to allow the oxidation of the primary alcoholic function. The oxidation product was washed with aqueous bicarbonate to remove the acidic fraction, and the neutral fraction was then subjected to gas-liquid chromatography.

Alkyl aryl ketones

All the alkyl aryl ketones used throughout this investigation were prepared by Friedel-Crafts acylation reactions according to standard procedures (Gilman & Adams 1961).

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استرات احماض آريل أوندىكانويك الايسومرية

نامق فرحات عويس
قسم الكيمياء بجامعة الكويت

خلاصة

تم تكاثف ميثيل أونديسنوات وكحول الأونديسنيل مع ألكيلات وهاليدات البنزين المختلفة في وجود حمض لويس ، ثم تمت أكسدة النواتج بحمض الكروميك الى ألكيل آريل كيتونات . عند تحليل نواتج الاكسدة بواسطة التحليل الكروماتوجرافي (غاز- سائل) وجد انها تتكون من خليط من ستة أيسومرات يتراوح موضع اتصال مجموعة الأريل بالسلسلة البارافينية فيها بين ذرات الكربون ٥ ، ١٠ .

