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IDENTIFICATION OF AN ALKYL GROUP AND ITS POSITION IN AROMATIC SUBSTANCES BY REACTION GAS CHROMATOGRAPHY

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SUMMARY

A method of identifying alkyl groups and their positions on an aromatic nucleus has been developed. A total of four methods, combining catalytic splitting with the identification of cleavage products by gas chromatography, were used. The type of alkyl is determined by catalytic degradation using a Leuna WK 9063 catalyst; their position in the presence of other functional groups is determined either by decarboxylation in quinoline, by desulphonation with sulphuric acid, by partial catalytic hydrogenation of the hydroxy group, or generally by distillation with zinc powder

INTRODUCTION

The identification and determination of the position of an alkyl group on an aromatic nucleus frequently represents a problem which is not easy to solve. One method, imperfect from to-day's point of view, is the determination of the alkyl-group content in the molecule by modification of the method of KUHN AND ROTH[1,2]. The latter is based on oxidation of the alkyl group by a mixture of sulphuric acid and chromic acid; the ensuing acetic acid being determined by volumetric analysis. However, this method provides no information on the type of alkyl group in question. A more recent method does, however, at least partly answer this problem[3]. It is based on an oxidative cleavage which is regulated to give various acid cleavage products of the alkyl group, which are then identified by paper chromatography. During this oxidation all the acids formed begin with C_{n-1} and go to acetic acid, so that it is not possible to differentiate between methyl and ethyl groups. A further improvement is a method which exploits destructive cleavage with a palladium catalyst[4]; the hydrocarbons produced are identified by gas chromatography. Unfortunately, this method has only been tested with a few aromatic hydrocarbons and identification of an alkyl group in an aromatic substance which contains other functional groups, *e.g.*, –COOH, –OH, –CHO, SO_3H, NH_2, etc., is usually required. One method reported uses decarboxylation[5,6] and the remaining hydrocarbons are identified by either mass or IR spectroscopy.

To solve this problem the authors made two approaches. They tried to develop

a method of identifying the alkyl group on the one hand, and to remove other functional groups from the aromatic nucleus on the other hand. In the course of applying these methods, products are created which were identified by gas chromatography.

The identification of an alkyl group on the aromatic nucleus was successfully carried out by hydrogenation cleavage using Leuna WK 9063 catalyst.

The position of the alkyl group could be determined by identifying hydrocarbons from their elution times using gas chromatography. In order to obtain these hydrocarbons, however, if the substance in question is not already a hydrocarbon, it is necessary to remove the other functional groups. A general universal method is pyrolytic destruction with zinc powder[7], whereby it is possible to remove nearly all oxygenic functional groups. Owing to its results not always being specific, this method was supplemented by other methods, *viz.* decarboxylation in quinoline in the presence of cupric salts; desulphonation by sulphuric acid and by the removal of the hydroxy group by partial catalytic hydrogenation on iron shavings.

IDENTIFICATION OF ALKYL GROUPS

As mentioned in the introduction, the authors used catalytic cleavage for identifying the alkyl groups, carried out immediately ahead of the chromatographic column. The cleavage products were fed directly to the gas chromatograph and identified by means of their elution times. Alkanes and alkenes, which form the most substantial part of these products, were of the greatest interest.

Experimental

Fig. 1 illustrates the equipment with which the dealkylation is carried out. Basically it consists of a quartz tube (1), 4 mm in inner diameter and 10 cm in length, which is widened at its upper end and fitted with a rubber stopper (4) of the type usually used for penicillin bottles. The tube is filled with Leuna WK 9063 catalyst (2)

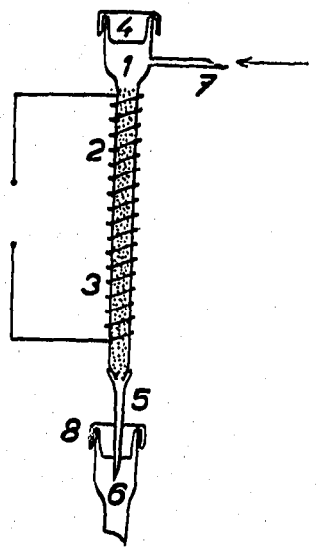

Fig. 1. Dealkylation equipment. For explanation see text.

(aluminium silicate SiO_2–Al_2O_3 = 60:40, impregnated with 4.5% WO_3 and MoO_3). The part of the tube holding the catalyst is heated by a resistor wire (3), the input of which is regulated to give an optimum temperature of 620°. The lower end of the tube terminates in a hypodermic needle (5). This needle passes through the stopper (8) and connects the tube (1) with the head of the chromatographic column (6). The hydrogen, which is simultaneously used as the carrier gas, is fed in through an inlet connected to branch (7). The sample is injected by means of a hypodermic needle through stopper (4) either in its natural form or as a suitable solution.

The chromatographic column, 140 cm in length and 4 mm in diameter, is filled with silica gel and operates at a temperature of 100°. A flame-ionization detector is used; the H_2-flow is 2 l/h; the sample dose is 5 μl. The elution order of the cleavage products is as follows: methane, ethane, ethylene, propane, propylene, butane, butylene, etc.

Results and discussion

Catalytic reductive cleavage was carried out on a wide variety of organic substances and the summary of results is given in Table I, where it can be seen that the reduction results in the formation of alkanes and alkenes. These correspond to the highest alkyl in the molecule, but at the same time all the hydrocarbons ranging down to methane are formed. This is due to the bonds of the carbon chain being roughly equivalent and to their cleavage at all positions in the chain. However, the proportions of the hydrocarbons produced are not quite arbitrary, although they vary slightly from case to case. In this way it is possible to tell whether a hydrocarbon was produced by cleavage of the carbon chain corresponding to a certain alkyl, or by the presence of another alkyl, or only by impurities. This ratio was investigated briefly with respect to aromatic hydrocarbons and phenols and it was found that: CH_4:C_2H_6 = 2.6; C_2H_6:C_3H_8 = 1.1; C_3H_8:C_4H_{10} = 2.6; if computed from the areas of elution curves of the chromatogram (Fig. 2). This ratio varies by a maximum of about ± 30%, but it never changes by an order of magnitude.

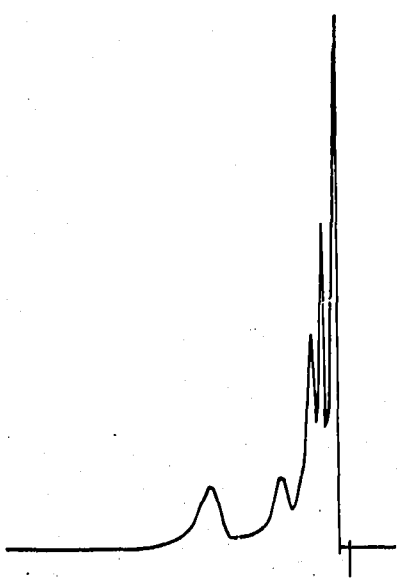

Fig. 2. Chromatogram of cleavage products of dealkylation. Highest alkyl group: propyl.

TABLE I

CATALYTIC CLEAVAGE OF ALKYL GROUPS[a]

For conditions see text.

	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_{10}	C_4H_8
Toluene; *o*-, *m*-, *p*-xylene; durene; prehnitene; 1,3,5- and 1,2,3-trimethylbenzene; dimethylnaphthalene; methylnaphthalene	+++	—	—	—	—	—	—
Ethylbenzene; *o*-, *p*-ethyltoluene	+++	++	++	—	—	—	—
Isopropylbenzene; *n*-propylbenzene	+++	++	++	++	++	—	—
Isobutylbenzene; *n*-butylbenzene; *sec.*-butylbenzene; *tert.*-butylbenzene	+++	++	++	++	++	+	—
m-, *o*-, *p*-Cresol	+++	—	—	—	—	—	—
m-Ethylphenol; 3,5-methylethylphenol; *p*-ethylphenol; 4,2-methylethylphenol; 2,5-diethylphenol	+++	++	++	—	—	—	—
p-Propylphenol; 2,5-ethylpropylphenol	+++	++	++	++	++	—	—
2-*n*-Butylphenol; 4-butylphenol; 2,4-di-*tert.*-butyl-6-cresol; 2,4,6-tri-*tert.*-butylphenol; 2,4-di-*tert.*-butylphenol	+++	++	++	++	++	+	—
Methanol	+++	—	—	—	—	—	—
Ethanol	+++	+++	+++	—	—	—	—
n-Propanol; isopropanol	+++	++	++	+++	+++	—	—
n-Butanol; *tert.*-butanol; butyl acetate	+++	++	++	+	+	++	++
Isopropylphenylether	++	+	+	++	++	—	—
Ethylphenylether	++	+++	++				
p-Xylidine; N-dimethylaniline	++++	—	—	—	—	—	—
N-Ethylaniline; N,N'-diethylaniline; ethylbenzylaniline	+++	++	+	—	—	—	—
Dimethyldichlorosilane; trimethylchlorosilane	+++	—	—	—	—	—	—
AAA[b]	++++	+++	+	—	—	—	—
BBB[c]	+++	++	—	—	—	—	—
Dipropyldichlorosilane	+++	++	+	++	+	—	—
Isobutyltrichlorosilane	++	+	+	+	+	+	—

[a] The number of crosses indicates the approximate ratio of cleavage products produced.

[b] For AAA read: methyltriethoxysilane; divinyltetraethoxysilane; methyldiphenylethoxysilane; triphenylethoxysilane; vinyltriethoxysilane; *p*-chlorobenzyltriethoxysilane; *p*-chlorophenyltriethoxysilane, methylphenyldiethoxysilane.

[c] For BBB read: tetraethylsilane; diethyldichlorosilane; ethyltrichlorosilane; ethyldichlorosilane; tetravinyltetramethyltetrasiloxane; triphenylvinylsilane; tribenzylvinylsilane; vinyltriethylsilane; trimethylvinylsilane; methylvinyldiethylsilane; methylvinyldiphenylsilane; trimethylalkylsilane; dimethylalkylsilane.

The production of an alkane and/or an alkene in the course of cleavage can also help to differentiate between different bonds. For example it was found that provided the alkyl in organosilicon substances is bound directly to the silicon atom, alkenes are not formed. However, if it is bound to oxygen, alkenes are formed. If a larger number of compounds were studied, it would surely be possible to find other connections.

The effect of temperature is also interesting. If the temperature is decreased, only the higher alkyls are subject to cleavage. For example, 1,2,4-trimethyl-5-isopropylbenzene at 200° only yields propane as the cleavage product; at 300° propane and propene, little propane being present; at 400° propane and propene; at 500° propene, propane, ethylene, ethane; and at 600° propane, propene, ethylene, ethane and methane. With ethylbenzene the first traces of ethylene and ethane appear at 400° (temperatures of 250 and 300° yielding no reaction).

Bearing this in mind and that in an identification there is no way of telling in advance which alkyl is being considered, a temperature of 620° was chosen so that all groups, including methyl groups, were subject to cleavage. However this phenomenon can be used in some cases for achieving a higher accuracy of the results.

INVESTIGATION OF THE POSITION OF THE ALKYL GROUPS OF AROMATIC ACIDS BY DECARBOXYLATION

The method is based on being able to carry out, under certain conditions, the removal of the carboxyl group while preserving the alkyl groups on the aromatic nucleus[5,6]. The residual hydrocarbon is identified by gas chromatography.

Experimental

The decarboxylation was carried out in boiling quinoline in the presence of cupric carbonate.

In a 20 ml flask 50 mg of sample is placed; 2 ml of quinoline and 200 mg of cupric carbonate are added, and this is carefully boiled under a reflux condenser

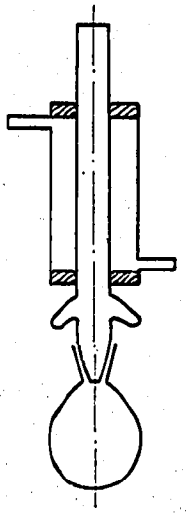

Fig. 3. Decarboxylation equipment.

(Fig. 3), which is fitted with a rim receiver for collecting the hydrocarbons formed. These are sampled by a Hamilton injection syringe and a 5 μl sample is fed into a Chrom 2 gas chromatograph.

The chromatography is carried out in a capillary column, 45 m in length, 0.2 mm in inner diameter. Apiezon L constitutes the stationary phase. A 10% solution of toluene is used for impregnation. The column temperature is 110°, the hydrogen flow rate 45 ml/min, the air flow rate 1 l/h, and the nitrogen carrier gas flow rate 2 l/h. The hydrocarbons are identified by means of the elution times as usual.

Results and discussion

The method was first tested with model substances (Table II), which showed that although the cleavage products with different aromatic carboxylic acids (or esters) differ, nevertheless the generation of the appropriate hydrocarbon is specific.

TABLE II

AREA BOUNDED BY THE CHROMATOGRAPHIC PEAK OF AN AROMATIC HYDROCARBON CREATED BY DECARBOXYLATION OF 50 mg OF ACID

Phthalic acid = 10.

Acid/Ester	*Benzene*	*Toluene*	*Acid/Ester*	*Benzene*	*Toluene*
Phthalic	10		Monomethylterephthalate	0.5	
Terephthalic	7		Methyl *o*-toluate		11
Isophthalic	2		Methyl *m*-toluate		7
Benzoic	6		Methyl *p*-toluate		20
o-Toluic		15	Methyl ester of *p*-aldehydobenzoic acid	traces	
p-Toluic		12	Dimethylphthalate	2	
m-Toluic		5	Dibutylphthalate		
5-Methylisophthalic		15	Dioctylphthalate		
Dianhydride of pyromellitic acid	0.5		Dinonylphthalate	0	
Anhydride of trimellitic acid	traces		Diethylphthalate		
Trimellitic	traces		*o*-Aldehyde of benzoic acid	5	
Dimethylterephthalic	1				

Furthermore, in some special cases an identification can be made because the amount of the hydrocarbon formed depends on the position and the number of carboxyl groups. This method was used to a special advantage in determining the presence of dimethylphthalic and methyltrimellitic acids in a mixture of carboxylic acids, in which isomeric xylenes were formed in addition to toluene. It was also found that aromatic aldehydes behave basically like benzene carboxylic acids.

DESULPHONATION

It is known that it is possible to remove a sulpho group from an aromatic nucleus with 50% sulphuric acid or phosphoric acid under pressure. This method was, therefore, used for identifying aromatic sulpho acids with varying numbers of methyl groups in various positions. The hydrocarbons formed were again determined by gas chromatography.

Experimental

Desulphonation. 40 mg of the sample is inserted into a thick-walled, roughly 2 ml ampoule and 1 ml of 50% H_2SO_4 is added, the ampoule is sealed and kept in a boiling water bath for 1 h. After the ampoule has been opened 0.5 ml of ether is added with which the hydrocarbons liberated are extracted; 2 drops of water are added, to facilitate the separation of the ether from the acid layer. 0.5 μl aliquots of the ether layer are used for injection into the gas chromatograph.

Chromatography. The aromatic hydrocarbons formed after desulphonation are identified by gas chromatography in the same way as described after decarboxylation.

Results and discussion

The desulphonation, under the conditions described, takes place smoothly and the results of the cleavage are given in Table III. In the case of the splitting of 2,3,5,6-tetramethylbenzenesulphonic acid, as well as tetramethylbenzene, a small amount of trimethylbenzene was also formed; the investigation of the purity of the original sulpho acid by paper chromatography did not establish the presence of the corresponding impurity.

TABLE III

DESULPHONATION OF AROMATIC SULPHO ACIDS

The numbers denote the relative ratios of the chromatographic peak areas (RRCPA).

Acid	*Cleavage product*	*RRCPA*
2,4,5,6-Tetramethylbenzenesulphonic	2,3,4,6-Tetramethylbenzene (isodurene)	21
2,3,4-Trimethylbenzenesulphonic	1,2,3,-Trimethylbenzene	60
2,3,4,5-Tetramethylbenzenesulphonic	1,2,3,4,-Tetramethylbenzene (prehnitene)	35
2,4,5-Trimethylbenzenesulphonic	1,2,4,-Trimethylbenzene	33
2-Methylbenzenesulphonic	Toluene	29
4-Methylbenzenesulphonic	Toluene	12
2,3,5,6-Tetramethylbenzenesulphonic	1,2,4,5,-Tetramethylbenzene (durene)	19

CATALYTIC HYDROGENATION OF PHENOLS

In order to obtain the appropriate hydrocarbon from alkylphenols, it is necessary to carry out partial hydrogenation of the compound (*i.e.* only the hydroxyl group). It is known that this hydrogenation is difficult with phenols. One method which yields the hydrocarbon is to pass the phenol over activated carbon or iron shavings at red heat[8]. Activated carbon could not be used in this case, because it holds up the hydrocarbon for some time and the chromatographic peaks obtained in this way tend to trail. Therefore, iron shavings were used, as they do not have this undesirable property.

Experimental

The catalytic hydrogenation of phenol is carried out with the same equipment

used for identifying alkyl groups (Fig. 1). Only the filling in the quartz tube is different, *viz.* iron shavings (cast iron), size 0.5 mm, from which traces of oil have been removed. The operational temperature is between 550 and 600°. The carrier gas is again hydrogen, flow rate 2 l/h.

The sample is fed into the apparatus by an injection syringe in its natural form or as an ether solution. The dose corresponds to 1 μl of phenol. The identification of the aromatic hydrocarbons is carried out in the usual way.

Results and discussion

The catalytic hydrogenation of an alkyl phenol yields the corresponding aromatic hydrocarbon. The reaction under the experimental conditions described affects only about 20% of the sample, the remainder of the alkyl phenol being eluted from the chromatographic column after the hydrocarbons. An attempt was made to increase the percentage conversion by changing the catalytic-layer temperature, but without success. It would have been necessary to extend the catalyst layer. However, as the same equipment was used as in the case of identifying alkyl groups and as the presence of the unreacted alkyl phenol does not hinder the identification, the operational conditions were not changed.

In the course of partial catalytic hydrogenation, apart from the appropriate alkyl benzene, a small amount of other cleavage products are also formed. These are lower aromatic hydrocarbons, which do not interfere with the identification, as their content is very much smaller than that of the principal component.

DISTILLATION WITH ZINC POWDER

One of the methods used for the cleavage of various functional groups (especially oxygenic), while preserving the methyl groups on the aromatic nucleus, is the distillation of the sample with zinc powder[7]. This method was used to determine the positions of the alkyl groups, although in some cases the determination is not specific.

Experimental

Cleavage with zinc powder was carried out with the equipment shown in Fig. 4.

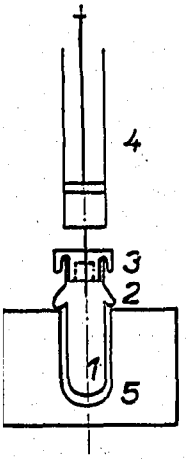

Fig. 4. Zinc powder distillation equipment. For explanation see text.

TABLE IV

CLEAVAGE PRODUCTS AND THE RELATIVE AREAS BOUNDED BY THEIR CHROMATOGRAPHIC PEAKS

	Benzene	*Toluene*	*m,p-Xylene*	*o-Xylene*	*Others*
Benzoic acid	302	1			
Trimellitic acid	0.8	0.9			
Phthalic acid	10	50			
Terephthalic acid	52	10			
Isophthalic acid	197	394			
o-Toluic acid		289			
p-Toluic acid		2830			
m-Toluic acid		700			
Monomethylterephthalate	1	60	3	2	
Dimethylterephthalate	8	14			
Methyl *p*-toluate		378	6	2	
Dimethylphthalate	230				
Dinonylphthalate	350				
Dianhydride of trimellitic acid	1	2			
p-Toluenesulphonic acid	0.5	18			
2,3,4,5-Tetramethylbenzenesulphonic acid					Prehnitene, 17
2,3,4-Trimethylbenzenesulphonic acid					1,2,3,-Trimethylbenzene, 10
2,4,5-Trimethylbenzenesulphonic acid					1,2,4-Trimethylbenzene, 2
p-Toluenesulphochloride		200			
m-Tolunitrile	5	12			
Terephthalodinitrile	7	12			
Isophthalodinitrile	15	1			
Phthalodinitrile	7	1			
Chlorobenzene	5				
o-Dichlorobenzene	traces				
Iodobenzene	99				
1,2,4-Trichlorobenzene	20				
3-Hydroxybenzaldehyde	6				
4-Aldehydo-1-methylbenzoate	2				
2,4-Diaminotoluene	3	9			
p-Xylidine			10		
o-Nitrobenzaldehyde	20				
o-Aminobenzoic acid	2				
p-Methoxybenzaldehyde	5				
Benzaldehyde	128				
Aniline	30				

Basically this consists of an inclined test tube (1), about 10 cm long, fitted with a rim (2), which can be sealed by a rubber stopper (3) (as used for penicillin bottles). This stopper is penetrated by an injection syringe needle (4). The test tube is heated to the required temperature by the brass block (5).

The sample (0.1 g) is put into the test tube and 1 g of the zinc mixture is added (zinc + zinc dichloride + sodium chloride in the weight ratio 4:1:1). The test tube is then closed, the hypodermic syringe needle is inserted through the stopper and the apparatus is placed in the brass heating block. It is heated at 300° for 15 min. The more volatile compounds formed during cleavage are accumulated in the hypodermic

syringe, so that the sample can be fed directly from the syringe into the gas chromatograph. The less volatile samples are accumulated near the rim of the test tube, from which the sample can either be taken out directly by an injection syringe, or after dissolving in a suitable solvent. The injection syringe serves to collect the more volatile components of the cleavage, and in the reverse case only acts as a pressure equallizer when the test tube is heated to a higher temperature. The chromatographic separation of cleavage products for purposes of identification is carried out in the same way as in the previous cases (decarboxylation, etc.).

Results and discussion

Table IV gives the results of experiments with a variety of compounds. Alkyl phenols are not mentioned, as the hydroxyl groups did not cleave on distillation with zinc. This also applies to most nitro substances, where complete destruction ensued. As can be seen from Table IV, the cleavage is not always to one compound and, furthermore, the amount of hydrocarbon formed by the various compounds differs substantially. This fact, however, can be exploited for identification purposes, as well as for quantitative analytical purposes especially in those cases where the minor component of the mixture to be determined yields large amounts of hydrocarbons, in addition to that formed by the principal component in the cleavage; the principal component yielding only very little hydrocarbon. In some cases a small amount of by-product was also formed; however, in each of these cases it was clear that it was not the principal component which was under examination; the only exceptions are phthalic acid, isophthalic acid and dimethylterephthalate. In some cases, however, this might be due to small amounts of toluic acid impurities, which can only be proved chromatographically with difficulty when present in small concentrations.

The distillation with zinc was always carried out with the same amount of sample, in order to make it possible to compare quantitatively the effect of cleavage.

In order to be able to solve some of the doubtful cases, or to prove some of the findings, it is necessary to compare all the results obtained by all the methods described in this paper.

CONCLUSION

Although it is clear that the methods described in this paper will not always be capable of yielding absolutely reliable information on the kind and position of the alkyl group in a molecule, the authors are of the opinion that in many cases they represent a necessary adjunct to existing methods, which they themselves have found useful.

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