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THE SYSTEMATIC ANALYSIS OF ORGANOSILICON COMPOUNDS BY CHROMATOGRAPHIC METHODS. II

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SUMMARY

Further methods for detecting the presence of various functional groups and bonds in molecules of organosilicon compounds by using the method of reaction chromatography have been developed. Cleavage was carried out by using boron tribromide, potassium hydrogen sulphate, potassium persulphate, solid sodium hydroxide, metallic sodium, boron trifluoride and Leuna WK 9063 catalyst. Further, the identification of hydroxyl groups with 3,5-dinitrobenzoyl chloride was achieved, and detection with pyrene was used in the paper chromatography of organosilicon compounds.

INTRODUCTION

We recently published a paper[1] dealing with the systematic analysis of organosilicon compounds. Gas, paper and thin-layer chromatography were mainly used, and the cleavage products were used for the identification of various bonds and functional groups.

This paper is a continuation of that work and the same methods were used for the identification of further functional groups and bonds in organosilicon compounds.

CLEAVAGE WITH BORON TRIBROMIDE

It was found that some functional groups bound directly to silicon are removed by reaction with boron tribromide, especially alkoxy and phenyl groups. If the cleavage of an organosilicon compound with boron tribromide is carried out before the compound enters the gas chromatographic (GC) column, the occurrence of various cleavage products indicates the presence of certain functional groups.

Experimental

The cleavage of organosilicon substances is carried out in the usual way in a small glass reactor[1]. First, a layer of potassium bromide is introduced into the reactor; over this is spread a layer of a porous material (the Rysorb GC carrier was used). About 0.2 g of the organosilicon compound is absorbed into the porous material. The inside of the glass reactor is provided with a glass tube by means of which a mixture of sulphuric acid and boron trioxide can penetrate into the lower layer of potassium bromide. About 1 ml of this mixture[1] is added with a hypodermic syringe through the penicillin cap closing the reactor. The reactor is placed in a brass heating block heated to 130°. The boron tribromide formed reacts with the organosilicon compound and the reaction products are collected in another hypodermic syringe, which is used for injecting the sample directly into a gas chromatograph when a sufficient amount of the cleavage products has been formed.

The mixture of sulphuric acid and boron trioxide is prepared as described previously[1] for cleavage with boron trifluoride.

The GC of the cleavage products is carried out by using a column 3 m long

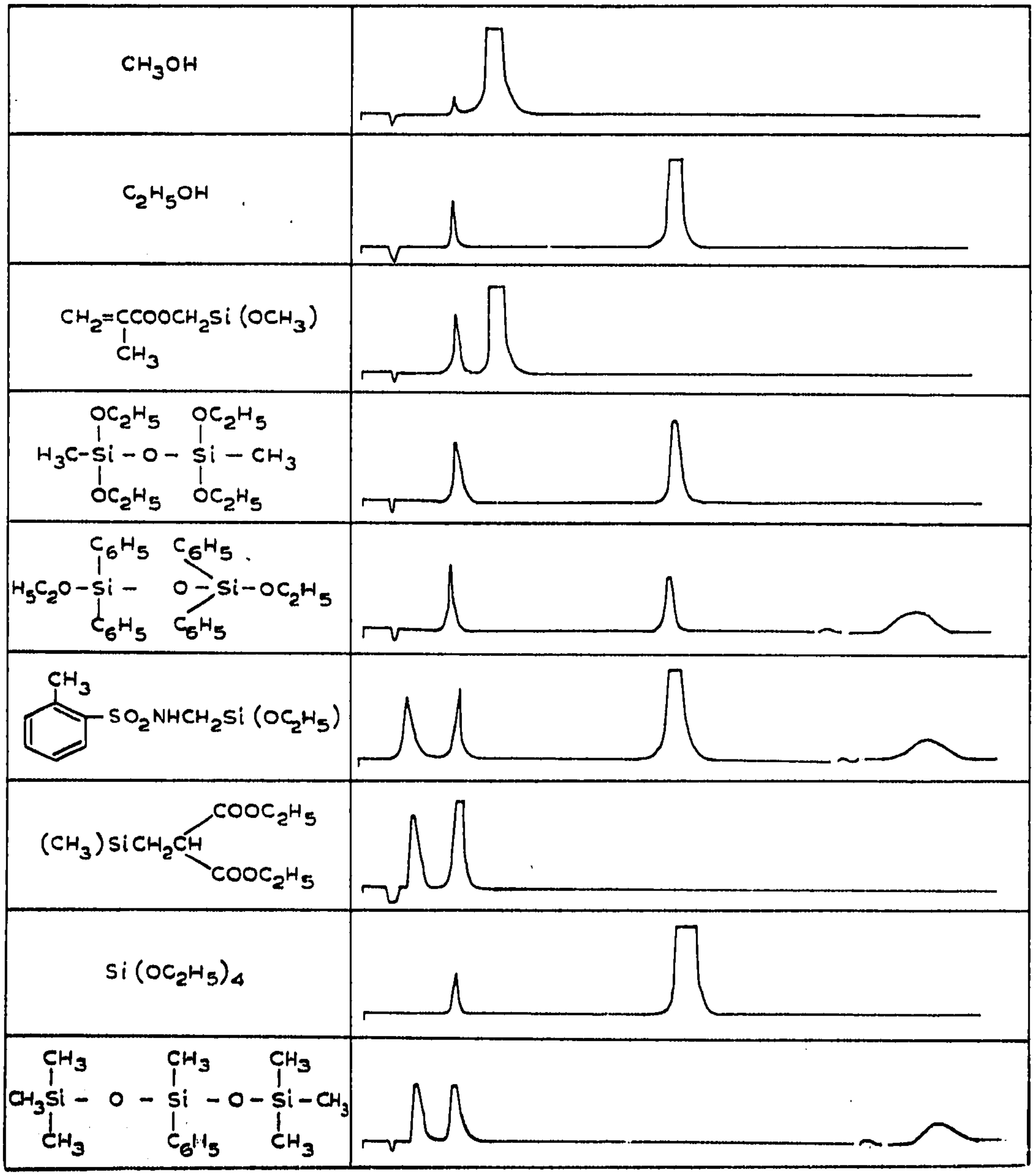

Fig. 1. Chromatograms obtained after cleavage of organosilicon compounds with boron tribromide.

and 4 mm in diameter, packed with Rysorb BLK and 10% of fluorinated silicon oil (FS-16, U.S.S.R.), at 25°. The flow-rate of the nitrogen carrier gas is 2 l/h.

Discussion

It follows from Fig. 1 that OR groups dissociate from organosilicon compounds; they are apparently first converted into the corresponding alcohols which react further, with formation of unidentified volatile compounds. It is possible to assume that certain alkyl groups are present on the basis of the elution times of these compounds. Besides alkyl groups, the phenyl group also dissociates as benzene, which also appears on the chromatogram.

Although the alkoxy and phenyl groups are usually detected by a different method (cleavage with hydroiodic acid, boron trifluoride and fuming nitric acid), the proof of their presence by another method provides a convenient supplement.

THE DISSOCIATION OF ETHYLENE OXIDE AND PROPYLENE OXIDE GROUPS BY POTASSIUM HYDROGEN SULPHATE

It is well known that, if a sample containing an ethylene oxide or propylene oxide chain is heated with potassium hydrogen sulphate, acetaldehyde and propionaldehyde, respectively, are formed. Organosilicon compounds containing such a chain behave in the same way.

Procedure

One or two drops of the sample (or a similar amount of a solid sample) are introduced into the reactor[1] and about a 50-fold excess of potassium hydrogen sulphate is added. The reactor is closed with a penicillin cap, placed in a heating block pre-heated to 260°, and left for 10 min at this temperature. A 10-ml hypodermic syringe is connected to the reactor. Vapour of the compounds liberated in the reactor is collected in the hypodermic syringe and, when the reaction is completed, is injected into a gas chromatograph.

The column is 160 cm long, I.D. 4mm, packed with Chezasorb and 20% of Carbowax 4000. Nitrogen is used as carrier gas and the column temperature is 20°.

Discussion

It was found that, during cleavage with potassium hydrogen sulphate, not only are the corresponding aldehydes dissociated, but also benzene is separated from the Si–Ph bond. A disadvantage is the fact that the acetone formed from isopropylene oxide groups has the same elution time as acrolein formed from glycerin, which may be bound to the compound being studied. Acetaldehyde is also formed if acetyl and ethoxy groups are present. The methoxy group yields formaldehyde.

In order to carry out the separation in some ambiguous cases, paper chromatography of the aldehydes formed, as their 2,4-dinitrophenylhydrazones, was carried out. Again, it is difficult to identify acetaldehyde in the presence of acrolein. The 2,4-dinitrophenylhydrazones are prepared as follows. From the hypodermic syringe, a portion of the cleavage products is introduced, by slow bubbling, into a solution of 2,4-dinitrophenylhydrazine in hydrochloric acid.

The R_F values of the aldehydes, with dimethylformamide as stationary phase and cyclohexane as mobile phase, were as follows: formaldehyde, 0.18; acetaldehyde, 0.39; propionaldehyde, 0.65; *n*-butyraldehyde, 0.87; and acrolein, 0.40.

As already mentioned, acetaldehyde is also liberated from the ethoxy group. To distinguish the ethoxy group in the presence of the ethylene oxide group, cleavage with potassium persulphate can be used as described below.

By cleaving the compounds with potassium hydrogen sulphate, hexamethyldisiloxane is formed from the $(CH_3)_3Si$ group, and is also recorded on the chromatogram.

The order of the elution times under the given operating conditions is as follows: acetaldehyde, propionaldehyde, acetone together with sulphur dioxide, hexamethyldisiloxane and benzene.

CLEAVAGE WITH POTASSIUM PERSULPHATE

Cleavage with potassium persulphate was chosen because it is possible to distinguish between some ambiguous cases that arise in the cleavage with potassium hydrogen sulphate. The main difference is that alkoxy and phenyl groups are not liberated by potassium persulphate and, on the other hand, the ethylene oxide and propylene oxide bonds yield identical products. In addition, the presence of the $-C=C-$ bond can be detected owing to the formation of ethylene.

Procedure

Several milligrams of a sample are introduced into the reactor[1] and an approximately 50-fold excess of solid potassium persulphate is added. The reactor is closed with a penicillin cap and placed in a heating block pre-heated to 260°. A 10-ml hypodermic syringe is connected to the reactor. Gaseous compounds collected in the syringe are, on completion of the reaction (after about 10 min), injected into a gas chromatograph.

The gas chromatograph has a column 160 cm long, I.D. 4 mm, packed with Chezasorb and 10% of Carbowax 4000. The detection is carried out with the Martin gas-density balance. The column temperature is 25° and nitrogen is used as the carrier gas.

The order of the components eluted is as follows: ethylene, acetaldehyde, propionaldehyde, sulphur dioxide.

Discussion

As already mentioned, cleavage with potassium persulphate enables components in some ambiguous cases in the cleavage with potassium hydrogen sulphate to be distinguished. Its great advantage is the formation of ethylene from carbon–carbon double bonds. It is obvious that ethylene is also liberated from vinyl and methacryl groups, and to a small degree, also from the phenyl group, if two of the groups are bonded to one silicon atom.

CLEAVAGE WITH SOLID SODIUM HYDROXIDE AT 200°

Cleavage with solid sodium hydroxide provides the possibility of detecting the presence of terminal $(CH_3)_3Si$ groups and, simultaneously, the Si–Ph group.

In addition to this, the presence of CH_3–Si groups, and the vinyl and allyl groups from which ethylene is liberated, can also be monitored.

Procedure

Into the reactor[1] (without the glass tube) are introduced several milligrams of the sample and to this is added about a 100-fold excess of solid sodium hydroxide. The reactor is closed with a penicillin cap and inserted into a heating block preheated to 200°. In a 10-ml hypodermic syringe, connected to the reactor, are collected the gaseous cleavage products and, after about 10 min, they are injected into a gas chromatograph. Because products with substantially different boiling points are monitored, two different sets of working conditions are used, as follows.

(a) A gas chromatograph provided with a thermal conductivity detector with a column 140 cm long, I.D. 3 mm, packed with Rysorb and 10 % of fluorinated silicon oil (FS-16). The operating temperature is 25° and nitrogen at a flow-rate of 3 l/h is used as the carrier gas.

(b) A gas chromatograph provided with a column 140 cm long, I.D. 3 mm, packed with active charcoal. The operating temperature is 25° and nitrogen is used as the carrier gas at a flow-rate of 3 l/h.

Discussion

It was found, during cleavage with solid sodium hydroxide, that $(CH_3)_3Si$ groups yield both $(CH_3)_3SiOH$ and $(CH_3)_3Si{-}O{-}Si(CH_3)_3$. These compounds are detected by GC under the conditions (a) above. In the same chromatograph, the presence of benzene, which is formed by the dissociation of Si–Ph groups, is also detected. During the cleavage of some organosilicon compounds, a strong odour resembling that of unsaturated hydrocarbons was observed, so a second GC separation was performed in which were identified methane, which is generally formed from the CH_3–Si group, and ethylene (or propylene), liberated by the dissociation of the vinyl (or allyl) group. Although all this information can also be obtained by some of the methods described earlier, we have chosen this procedure to support the previous findings.

THE DETECTION OF ACTIVE HYDROGEN

Besides the Si–H bond, the identification of which has already been described, some organosilicon compounds also contain an active hydrogen of a different kind. Active hydrogen can be dissociated by reaction with sodium.

Procedure

A small piece of sodium is introduced into the reactor[1] (without the glass tube), a small amount of benzene is added, and the reactor is closed with a penicillin cap and heated to 80°. It is flushed several times with dry air, until no hydrogen appears inside the reactor on repeated heating. Then several drops of the sample are added with a hypodermic syringe, and after 10 min the reactor is flushed with air and a sample is injected with a hypodermic syringe into a gas chromatograph. (In this way, the presence of active hydrogen released at a low temepratura is detected.) Then the reactor with the reaction mixture is heated to 80° and the whole procedure is repeated.

The gas chromatograph is provided with a thermal conductivity detector and a column 140 cm long, I.D. 3 mm, packed with active charcoal. The column temperature is 25°, the carrier gas (nitrogen) flow-rate is 3 l/h, and the presence of hydrogen is monitored.

Discussion

Because of the high sensitivity of the reaction, the results must be evaluated carefully, as organosilicon compounds may contain a little occluded water. On the other hand, they may also contain small residues of solvents that have been distilled off and which contain active hydrogen. Therefore, the results must be evaluated together with other results.

THE DETECTION OF THE PRESENCE OF SULPHUR

The presence of sulphur can be detected by the Lasseigne test or by two new techniques that have been developed in connection with the analysis of sulphur-containing organosilicon compounds.

The first of the two new methods is a general one and is based on the liberation of elemental sulphur with fuming nitric acid. The working procedure will not be given here, as it is identical with that described for the detection of organosilicon compounds containing the phenyl group by the action of fuming nitric acid[1]. This method was discovered when it was found that some compounds turn deep yellow during detection with fuming nitric acid. It has been found that almost all organic compounds containing sulphur undergo this reaction[2]. The yellow colour is due to the liberation of elemental sulphur.

In studies of organosilicon compounds, attention should be paid to aryloxy and chlorophenyl groups that may be present and which also yield yellow spots with fuming nitric acid.

The second method is based on the cleavage of organosilicon compounds with boron trifluoride. We found that boron trifluoride causes sulphur-containing organic compounds to yield mainly sulphur dioxide on heating in the presence of air.

Procedure

The procedure is identical with that described in the paragraph on cleavage with boron trifluoride, except that the GC of the cleavage products is carried out differently[1].

A gas chromatograph with a column 160 cm long, I.D. 4 mm, packed with silica gel, is operated at 150°. Before packing, the silica gel is activated at 250° for 8 h. The flow-rate of the nitrogen carrier gas is about 3 l/h.

Chromatograms of the cleavage products are given in Fig. 2.

Discussion

It is obvious from the chromatograms that sulphur dioxide is the main reaction product. Nevertheless, other sulphur compounds, such as carbon disulphide, hydrogen sulphide and carbonyl sulphide and also carbon dioxide, are formed, depending on the type of sulphur bonds present[2].

As far as can be judged from the few examples given and from a number of experiments carried out with sulphur-containing organic compounds (without silicon), carbonyl sulphide is most frequently formed when sulphur is bound as $=C=S$ and $—CH=S$. Sulpho, sulphoxy, and sulphoamido groups do not yield any cleavage products that contain sulphur. Also, sulphur bound to an inorganic group and elemental sulphur yield no cleavage products.

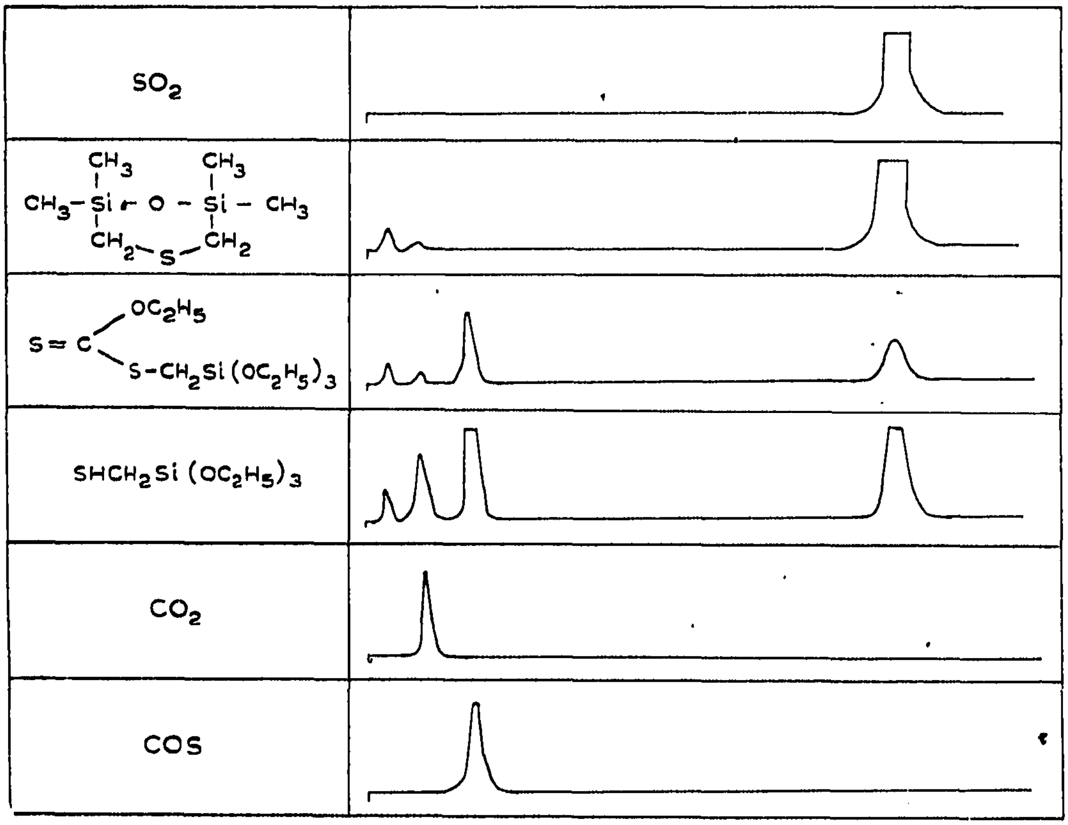

Fig. 2. Chromatograms obtained after cleavage of sulphur-containing compounds with boron trifluoride.

This procedure is, therefore, advantageous when it is required to determine whether the sulphur that has been detected by the Lasseigne test is bound in the organosilicon compound in the sample or is present only as an inorganic component.

In the GC, it is possible to work at 175°. Under such conditions, however, carbonyl sulphide will not be separated from hydrogen sulphide, or carbon disulphide from sulphur dioxide, or else they will be only partly separated.

THE DETECTION OF THE PRESENCE OF THE HYDROXYL GROUP

The detection of hydroxyl groups in organosilicon compounds is not as simple as it may seem, as the methods usually used are inapplicable in many cases. We attemped to use the reaction of the hydroxyl group with 3,5-dinitrobenzoyl chloride for this purpose but it had to be modified as the procedure usually used was unsatisfactory.

Basically, the reaction between the hydroxyl group and 3,5-dinitrobenzoyl chloride, followed by the detection of the reaction products by paper chromatography, is used.

Procedure

The sample (several milligrams) is heated to 200° with about a 2–3-fold excess of 3,5-dinitrobenzoyl chloride (which is kept in sealed ampoules), for about 5 min in a small glass tube. After cooling, the contents are diluted with a small amount of benzene, corresponding approximately to the volume of the melt. After the melt has dissolved in the benzene, the solution is transferred directly to Whatman No. 1 chromatographic paper, impregnated with formamide. Cyclohexane is used as the developing solvent. The detection is performed by spraying with Ehrlich reagent after preliminary reduction with stannous chloride (see the Chapter: "Alkaline hydrolysis")[1].

Discussion

As found during the development of the method, the reaction with organosilicon compounds takes place only in a solventless medium and at relatively high temperatures. The effect of boron trifluoride on the above reaction was examined and it was found that it causes almost no increase in the reaction rate.

The number of hydroxyl groups can be approximately estimated from the intensity of the spots on the chromatogram. If no hydroxyl groups are present, there is only a spot at the start. It must, of course, be borne in mind that sometimes the distillation residue analyzed may contain a small amount of a solvent that contains hydroxyl groups. For this reason, the solvent in which the sample was originally dissolved must always be considered.

The fact that the spots on the chromatogram are elongated is generally due to the presence of a mixture of a certain type, containing compounds having different molecular weights.

THE IDENTIFICATION OF THE CARBON CHAIN BOUND TO SILICON BY CLEAVAGE ON LEUNA WK 9063 CATALYST

Recently, a method for detecting alkyl groups bound to the carbon of the aromatic ring was developed[3] and it was found that the method is generally suitable for determining the length of a carbon chain in any compound. The method can generally be used for most types of organic compounds. For this purpose, catalytic hydrogenation on Leuna WK 9063 catalyst in a hydrogen medium is used. The cleavage products are alkanes and alkenes with the appropriate number of carbon atoms, and these are identified by GC.

Experimental

The apparatus for the above technique has been described elsewhere[3], and basically it consists of a quartz tube of length 10 cm and I.D. 4 mm, provided with an electrical resistor coil and closed with a penicillin cap. The tube is packed with Leuna WK 9063 catalyst (aluminium silicate, 60:40 SiO_2–Al_2O_3, impregnated with 4.5 % of tungsten (VI) and molybdenum (VI) oxides). The tube is connected directly to a gas chromatograph and hydrogen is passed through it, serving simultaneously as the carrier gas. The hydrogen inlet is in the side of the upper part of the tube. The resistor heats the catalyst to 620°.

The sample is placed in the upper part of the quartz tube with a hypodermic syringe. If a solid sample is used, it can be first dissolved in an inert solvent (*e.g.*, benzene).

The GC is carried out by using a column 140 cm long, I.D. 4 mm, packed with silica gel. The operating temperature is 100° and the amount of sample used is 5 μl. The order of the components eluted is as follows: methane, ethane, ethylene, propane, propylene, butane, butylene, etc.

Discussion

In most cases, all the alkanes and alkenes are formed by this catalytic reaction, from the highest number of carbon atoms downwards. For example, in the presence of –C–C–C–, propane, propylene, ethane, ethylene and methane, will appear in the chromatogram, while in the presence of the –C–C– bond, only ethane, ethylene and methane are formed. Further details can be found in the earlier paper[3].

In this way, the chain length of an organosilicon compound can be unambiguously determined, whether the chain is bound directly to a carbon atom or to another atom of the compound.

CLEAVAGE WITH BORON TRIFLUORIDE

In Part I[1], the cleavage of the siloxane bond with boron trifluoride was described. It was also found that, besides fluorosilanes, more cleavage products are formed having higher boiling points and which have not been identified. In this work, it was attempted to use these cleavage products in connection with GC for the identification of some more functional groups, such as $\equiv$Si–CH$_2$–Si, $\equiv$Si–CH$_2$CH$_2$–Si$\equiv$, –CH$=$CH$_2$, –CH$_2$CH$=$CH$_2$, CH$_2$CH$_2$CH$_2$O– alkyl and alkoxy groups.

Experimental

The cleavage is carried out in exactly the same way as described earlier[1], except that the heating block is heated to 180°.

It is obvious that the GC separation is somewhat different. A column 140 cm long, I.D. 4 mm, is used, packed with silica gel. The flow-rate of the hydrogen carrier gas is 3 l/h. The operating temperature for compounds up to C_3 is 75°, for C_4 120°, and higher if necessary.

Chromatograms are shown in Fig. 3.

Discussion

Although the identification of the cleavage products has not been carried out, it is nevertheless evident that, from their elution times, conclusions can be drawn concerning the presence of certain functional groups or bonds. It was also found that the results are not always unambiguous, but they provide additional information that can be compared with some of the previous results.

For example, the cleavage product with the shortest elution time (Fig. 3) is obtained from the configuration $\equiv$Si–CH$_2$–Si$\equiv$; it is followed by another product corresponding to the group C_2H_5O–, CH_2= CH–Si, $\equiv Si(CH_2)_2Si \equiv$ or –CH_2CH_2O–. An even higher elution time corresponds to the cleavage product corresponding to the $CH_2 = CHCH_2Si$–, C_3H_7– or –$CH_2CH_2CH_2O$– group.

If functional groups with even higher numbers of carbon atoms are subjected to the cleavage, the temperature of the column must be increased, *e.g.*, to 120° for C_4 compounds.

THE DETECTION OF ORGANOSILICON COMPOUNDS WITH PYRENE

Organosilicon compounds have generally not been detected by paper and thin-layer chromatography owing to their low reactivities. Recently, we found

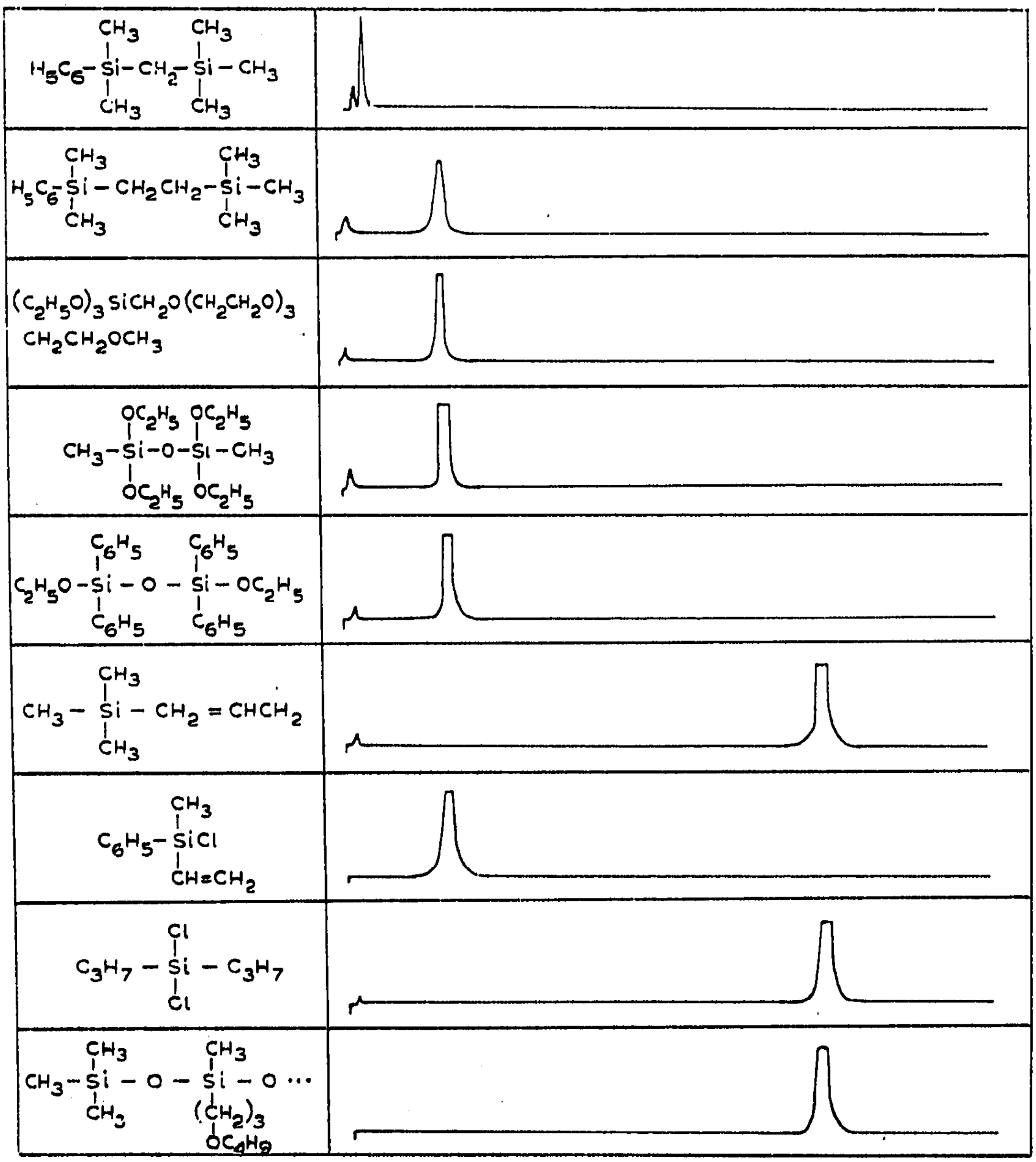

Fig. 3. Chromatograms obtained after cleavage of organisilicon compounds with boron trifluoride at higher column temperature.

a useful and sensitive detection technique[4] for those organosilicon compounds that contain the phenyl group bound to silicon, in which fuming nitric acid was used. Organosilicon compounds appeared as black spots.

A detection reagent has now been found for all types of organosilicon compounds, *viz.*, a spray reagent comprising an acetone solution of pyrene.

Experimental

The chromatogram (a paper or thin-layer support) is sprayed with a saturated solution of pyrene in acetone and is left in a drying box at about 50–60° until intense yellow-green fluorescent spots appear under UV light.

Discussion

This detection with pyrene is based on the fact that pyrene is more easily dissolved in the non-polar organosilicon component than in the support (paper or silica gel). This detection method was also checked with other non-polar compounds such as, for example, mineral oils, or even with compounds of medium polarity, such as esters. In all these cases, the detection was sufficiently sensitive.

The detection of organosilicon compounds with pyrene is very important as it is frequently required for separating various components of these compounds for micropreparations, and for identifications with cleavage reactions.

A strange phenomenon was observed in the detection with pyrene: if a chromatogram detected in this way is exposed to the vapour of fuming nitric acid, the spots for compounds that contain the $-OCH_2CH_2-$ or the $-OCH_2CH_2CH_2-$ group turn orange or even deep red.

PROOF OF THE PRESENCE OF ACETYL GROUPS

The presence of acetyl groups can be proved in organosilicon compounds by the hydrolytic liberation of acetic acid and by the detection of this acid by GC and paper chromatography.

Experimental

Hydrolysis is carried out with 1*N* sodium hydroxide solution, boiling the mixture under reflux for about 1 h.

The GC of the hydrolysate is performed with a column 3 m long, packed with Porapak Q. The column temperature is 190° and the carrier gas (nitrogen) flow-rate is 3 l/h.

Paper chromatography is carried out on Whatman No. 1 paper in the system *n*-propanol–ammonia (2:1). A saturated aqueous solution of 2,6-dichlorophenolindolphenol is used for the detection.

CONCLUSION

The methods for the identification of functional groups and bonds in organosilicon compounds by means of the reaction chromatography methods that have been developed represent another contribution to the problem. It is obvious that some of the given methods have a more general use, even in other branches of organic analysis.

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