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CATALYTIC SYNTHESIS OF ALKYLPHENOLS

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INTRODUCTION

The chemistry of phenols has developed rapidly during the last two decades. One of the lines of work in this field has been the synthesis of alkyl derivatives, the investigation of their properties, and the search for methods of effective application of the alkylphenols in industry.

Among the most important uses of alkylphenols, their application, due to their easy oxidisability, as antioxidants for aviation fuels[1-5], lubricants[6-9], various fats[10-13], natural rubber, synthetic rubber[13-17], and other organic compounds[18-23], is of interest. Alkylphenols are also used as depressors for lubricants[24-27], as starting materials for the preparation of herbicides and fungicides[28], bactericides[29], insecticides[30] and as disinfectants[31]. This list of examples of the practical application of the alkylphenols shows the wide prospects for their utilisation in the national economy.

In the present article an attempt is made to give a survey of the numerous investigations on the catalytic synthesis of alkylphenols, which possesses a number of advantages over other methods by virtue of the simplicity of the starting materials, the accessibility of catalysts, and the high yields of alkylated products.

Since the most frequently used starting materials are unsaturated hydrocarbons, alcohols and alkyl halides, it is useful to systematise the literature according to the nature of the phenolic substances being alkylated. In the individual sections, the subject is considered in relation to the catalysts, the nature of which to a considerable extent determines the structures and relationships of the alkylated products.

The catalysts are usually various acid agents: sulphuric, phosphoric, boric, hydrohalogenic, and perchloric acids, boron fluoride and its molecular compounds, zinc and aluminium chlorides, natural clays and industrial aluminium silicates, ion-exchange resins, aluminium phenoxide, etc.

I. ALKYLATION OF PHENOLS BY UNSATURATED HYDROCARBONS

1. The Use of Acids as Alkylation Catalysts

One of the first catalysts to find application in the alkylation of phenols by alkenes was sulphuric acid[32-34], which has been used in this reaction not only as such, but also in mixtures with other substances — acetic[32-37] and boric[38] acids, and also with salts, for example ammonium sulphate[39].

The quantity of sulphuric acid used has varied a lot. Thus, Koenings[32-34] used for the alkylation of phenols by isopentene and styrene ten volumes of a solution of 1 part of concentrated sulphuric acid in 9 parts of glacial acetic acid. However, in subsequent work, the quantity of sulphuric acid was considerably diminished, and at the present time it amounts to 3–10% of the weight of phenol[40-44].

Mamedaliev[42] investigated the influence of the quantity of sulphuric acid on the yield in the alkylation of *o*-cresol by alkenes. It was shown that the use of above 5% of the acid led to a reduction of the yield, particularly that of monoalkylated products.

In the literature there is no mention of the preparation of ethylphenols by the alkylation of phenol by ethylene in

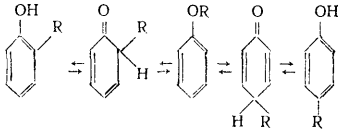
the presence of sulphuric acid. It was not until 1958 that Mamedaliev[42] carried out such an alkylation of *o*-cresol, but the ethyl-*o*-cresols were not isolated. Under the same conditions (140°–150°), alkylation of *o*-cresol by propene, n-butene, and isobutene gave monoalkylcresols in yields of 42, 51, and 55% respectively, and dialkyl-*o*-cresols in yields of 14, 15, and 17%.

As the alkenes of high molecular weight, and particularly those with a branched carbon chain, enter more easily into the alkylation reaction, and the products formed find a diversity of applications, the alkylation of phenols by butenes, pentenes, diisobutenes, etc. has been investigated in more detail. The temperature conditions for this reaction are very varied. In early papers[32-34] alkylation at room temperature is described; several days are required to complete the reaction and low yields of alkylphenols are obtained, the formation of the corresponding phenolic ethers being apparently favoured by the low temperature. In a series of later papers[45,46] it has been found that lowering of the temperature facilitates alkylation on the oxygen according to the following scheme[45]:

$$CH_3CH_2CH{=}CHCH_3 + H_2SO_4 \rightarrow CH_3CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HOSO_3H \xrightarrow{HOC_6H_4CH_3}$$

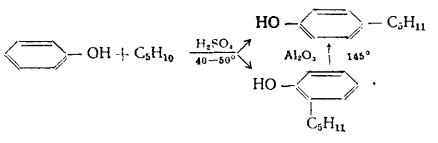
$$\rightarrow CH_3CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HOC_6H_4CH_3 + H_2SO_4.$$

Natelson[46] showed that the equilibrium phenolic ether $\rightleftharpoons$ $\rightleftharpoons$ alkylphenol set up in any alkylation process is displaced towards the formation of alkylphenol by a rise of temperature. Alkylation of phenol by an unsaturated hydrocarbon in the presence of sulphuric acid was begun at 0°–10°, and on raising the temperature to 65°, alkylphenols in yields up to 90% were obtained; the author considered that the increase in temperature isomerised the alkyl phenyl ether through a series of stages:



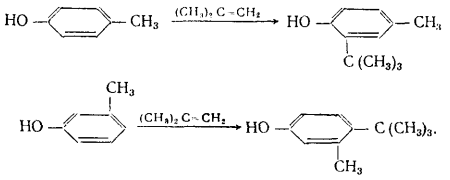
For this reason, for the direct formation of butyl- and pentyl-phenols a higher alkylation temperature is used, i.e. 40°–150°.[36,47-49]

The proportions of phenol to alkene depend on the nature of the desired product. With equimolar proportions of the original substances, the reaction results, usually, in the formation of the monoalkylphenol[44,48,50-54]. In the presence of an excess of alkene, di- and tri-alkylphenols are produced[40,47,54,55]. The orientation of the alkyl group is determined by the structure of the initial phenol and the temperature of the alkylation, as well as by the nature of the particular catalysts used. Thus, in the alkylation of phenol and of *o*-cresol by pentene at 40°–50°, a mixture of *o*- and *p*-isomers is formed[56,57], which, after prolonged treatment at a higher temperature (145°) in the presence of activated clay, gives the pure *p*-isomer[57]:

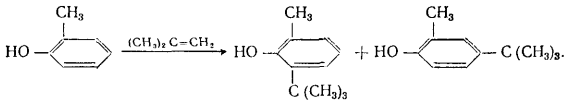


The formation of a mixture of *o*- and *p*-butylphenols is also observed in the alkylation of phenol by isobutene at 90°.[43] At a higher temperature (120°–150°) this reaction yields *p*-alkylphenol[58]. The nature and quantity of the isomers formed is also determined by the structure of the initial phenol[59,60].

Weinrich[59] investigated the structure of the isomers formed by the alkylation of cresols and xylenols by isobutene at 60°–70°. In this, *p*- and *m*-cresols form one monosubstituted t-butylcresol each, 4-methyl-2-t-butylphenol and 3-methyl-4-t-butylphenol, respectively:

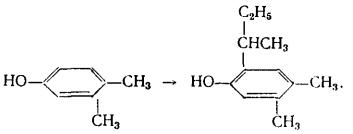


Under these conditions, *o*-cresol forms two monosubstituted products: 2-methyl-6-t-butylphenol and 2-methyl-4-t-butylphenol:



Stevens[61] accomplished a separation of isomeric cresols and xylenols by using the different solubilities, in alkali and in Claisen's solution, of the alkylphenols formed by the alkylation of the cresols and xylenols by isobutene in the presence of small quantities of sulphuric acid (3–5%). The author established a series of rules determining the position occupied by the tertiary butyl group. It was shown that the tertiary butyl group does not enter the ring between two methyl groups or between a methyl and a hydroxyl group; thus, 3,5-xylenol does not react with isobutene[61].

A characteristic peculiarity of the alkylation of phenols by alkenes in the presence of sulphuric acid is the tendency of the entering alkyl groups to isomerise in the following way: primary → secondary → tertiary. This isomerisation leads to a displacement of hydrogen atoms without alteration of the carbon skeleton. Thus, Albert[54], from the alkylation of 3,4-dimethylphenol by 1-butene, obtained 3,4-dimethyl-6-s-butylphenol:



Parker and Goldblatt[62] prepared 4-t-butylphenol from isobutene and phenol and also 4-t-pentylphenol by the alkylation of phenol by 2-methylbut-1-ene and by 2-methylbut-2-ene. Similar rules have been noted by the authors of a number of papers[33,40,42,43,45,58-60,63,64].

Ipat'ev, Pines, and Schmerling[65,66] established that the sulphuric acid isomerises alkenes in almost all cases when they are used for the synthesis of alkylbenzenes. The authors consider that the primary product of the reaction is a monoalkyl sulphate which, according to the conditions, can isomerise at a rate which depends on the structure of

the initial alkene. For example:

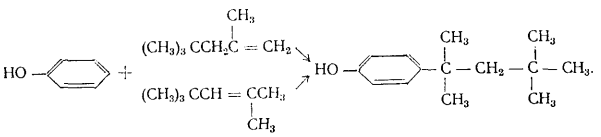
$$(CH_3)_2CHCH=CH_2 + H_2SO_4 \rightleftarrows (CH_3)_2\underset{\displaystyle SO_3H}{\underset{|}{C}}HCH_3,$$

$$(CH_3)_2\underset{\displaystyle SO_3H}{\underset{|}{C}}CH_2CH_3 \rightleftarrows [(CH_3)_2C=CHCH_3] + H_2SO_4.$$

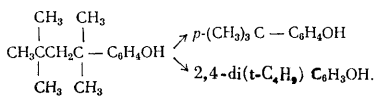
The sulphate formed may subsequently give carbonium ions:

$$(CH_3)_2\underset{\displaystyle SO_3H}{\underset{|}{C}}CH_2CH_3 \rightleftarrows (CH_3)_2\overset{+}{C}CH_2CH_3 + (SO_3H)^-.$$

When the rate of the isomerisation is low (for example in the case of 1-pentene) a mixture of alkylbenzenes is formed. However, in the case of isopentene the rate of the isomerisation is sufficiently high for the formation of only t-pentylbenzene. Apparently the above scheme of the alkylation of benzene applies also in the alkylation of phenols by alkenes. The phenomenon of the isomerisation of the entering radical is observed also in the alkylation of phenols by mixed isobutene dimers, 2,4,4-trimethylpent--1-ene and 2,4,4-trimethylpent-2-ene. Niederl[67] has shown that the reaction of diisobutene with phenol (temp. 10°–50°, 5% sulphuric acid) yields the *p*-isomer, i.e. 2-(*p*-hydroxyphenyl)-2,4,4-trimethylpentane, or *p*-t-octylphenol:



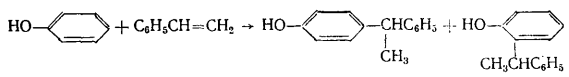
In spite of the low reaction temperature, the author[67] did not succeed in isolating the t-octyl ether of the phenol, in agreement with Ipatieff's results[68]. The latter established that *p*-t-octylphenol appears as the product of this reaction only when a low temperature and small quantities of sulphuric acid are used. At a higher temperature (85°) and in the presence of large quantities (~ 20%) of sulphuric acid, *p*-t-butylphenol is obtained, for the formation of which Ipatieff suggests the following scheme:



The correctness of this scheme was confirmed by the formation of *p*-t-butylphenol and 2,4-di-t-butylphenol by heating *p*-t-octylphenol with phosphoric acid to 140° in a sealed tube. Under conditions similar to those described by Niederl and other authors[69-71], *p*-t-octylphenol was prepared. The corresponding *p*-octyl substituted derivatives of the cresols[71,72] and of the dihydric phenols[71,73] were prepared under analogous conditions.

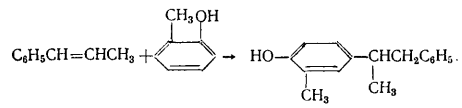
In addition to acyclic hydrocarbons, terpenes[74] and aromatic hydrocarbons with an unsaturated side chain, e.g. styrene[32,75-77] and 1-phenylprop-1-ene[78] have been used for the alkylation of phenols in the presence of sulphuric acid. Frisch[76] condensed phenol with styrene in the presence of small quantities of sulphuric acid (~ 1%). To be successful, this reaction requires a sufficiently high temperature (120°–200°) and a large excess of the original phenol (phenol : styrene = 4 : 1 [76] and 7 : 1.5 [77]), which decreases the polymerisation of the styrene to a minimum.

In this way, the total yield of substituted phenols reaches 75–85%; [76] the product consists of a mixture of *o*- and *p*-(α-phenylethyl)-phenols in the molar ratio 3 : 2:



High yields of α-phenylethylphenols of the order of 85–90% were obtained by Buu-Hoï[79] by the alkylation of phenol and also *o*- and *p*-cresols by means of styrene. The reaction was carried out at 100°; a reduction in the degree of polymerisation was achieved by the dilution of the reaction mixture with toluene, thus avoiding the use of a large excess of phenols.

Niederl[78] reacted α-phenylpropene and the isomeric cresols. The reaction gave the corresponding 1-phenyl--2-hydroxy(methylhydroxyphenyl)propanes, e.g. with *o*-cresol 1-phenyl-2-(4-hydroxy-3-methylphenyl)propane was obtained:



Apart from numerous alkenylbenzenes, 2-phenylbut-2-ene and 2-phenylpent-2-ene have been used in this reaction under the conditions described[80].

Certain sulphonic acids have been suggested as catalysts in the alkylation of phenols by alkenes. Proell[81] used C_1-C_3 alkylsulphonic acids in this reaction. These catalysts can promote the polymerisation of the original alkene at a temperature of the order of 70°. The author prepared octylphenol in 98% yield, dodecylphenol (68%) and pentadecylphenol (78%), using a catalyst of 91% RSO_3H + + 3% H_2SO_4 + 6% H_2O and the individual alkenes or their polymers as alkylating agents.

Wuyts patented the use of *p*-toluenesulphonic acid as catalyst in the synthesis of limonylphenol[82]. Kitchen[83] used benzenesulphonic acid for the synthesis of terpenylphenols. He obtained 2,4-dimethyl-6-isobornylphenol (35%) by the reaction of camphene with 2,4-dimethylphenol in toluene solution at 129°–130°. In certain cases, the sulphonic acid derivative of the phenol to be alkylated may serve as catalyst. For example, equimolar quantities of the cresol fraction and sulphuric acid were mixed; to the cresol sulphonic acid formed a fresh portion of the cresol fraction was added, the water evolved in the reaction was boiled off at 120°, and the butene dimer was added. The yield of octylcresols amounted to 86% [72,84].

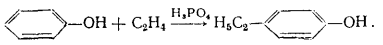
In the patent literature the use of fluorosulphonic acid in the alkylation of phenol by isobutene and diisobutene is mentioned[85]. On carrying out the reaction between phenol and isobutene in benzene solution at 25° in the presence of fluorosulphonic acid, *p*-t-butylphenol is formed almost exclusively in 84% yield with only 2.5% of the corresponding *o*-isomer; the action of this catalyst is thus essentially different from that of sulphuric acid under the same conditions[56,57].

In recent years, alkylphenols have been prepared in high yields by the use of cation-exchange resins of the sulphonated-polymer type as catalysts[86-88]. Thus, Loev[86] prepared nonylphenol, *p*-t-octylphenol and *p*-t-butylphenol in yields of 90, 73, and 88% respectively, by the alkylation of phenol in the presence of Amberlite by 1-nonene, diiso-

butene, and isobutene at 100°–110° at atmospheric pressure. Boisselet and Parc[88] used sulphonated polystyrene resins as catalysts. They prepared 2-t-butyl-*p*-cresol in 62% yield.

Isagulyants[89] used the KU-1 cation-exchange resin (a sulphonated phenol-formaldehyde polymer) and KU-2 resin (a sulphonated copolymer of styrene and butadiene) in the alkylation of phenols. At a reaction temperature of 90°–140° he obtained high yields (75–99%) of *p*-alkylphenols by the alkylation of phenol by isobutene, isopentenes, octene, styrene, etc. It is interesting to note that this author did not isolate polyalkylated products, the formation of which has been reported by workers who had used cation-exchange resins[88].

Phosphoric acid has been used much less than sulphuric acid as catalyst in the alkylation of phenols by unsaturated hydrocarbons. To a considerable extent this is explained by the greater accessibility of the latter, and sometimes also by the lesser effectiveness of phosphoric acid in the reaction[68,79]. Ipat'ev[90] succeeded in preparing ethylphenol in a yield of 43% by the alkylation of phenol with ethylene in the presence of phosphoric acid in the autoclave at 225° and a pressure of 80–95 atm. As phenetole does not isomerise under these circumstances, the reaction does not go via the formation of the ether, but takes place by direct alkylation of the nucleus:



Together with Pines and Komarevskii, Ipat'ev[90] carried out the alkylation of phenol by propene under normal and increased pressures. In both cases isopropylphenol was isolated.

Isagulyants similarly prepared isopropyl-t-butylcresols and the corresponding ethers by the alkylation of *m*- and *p*-cresols with propene and isobutene[91]. The alkylation of cresols[92,93], guaiacol[94], and dihydric phenols[95,96] by alkenes in the presence of phosphoric acid has been described.

In the literature the use of mixed catalysts for alkylation is mentioned, for example oxides or acids derived from boron mixed with organic dibasic acids or their alkyl esters[97].

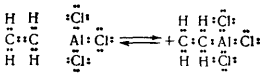
Apart from the acids mentioned above, certain halogen compounds, chiefly the hydrogen halides, are used as catalysts in alkylation. Thus, Stoermer[98] reacted styrene with phenol in the presence of hydriodic acid. The chief product was *p*-hydroxydiphenylethane with an insignificant admixture of the *o*-isomer; this is apparently connected with the greater stability of the *p*-isomer under these conditions. It was shown that under these conditions the *o*-isomer is transformed into the *p*-isomer. Calcott[99] alkylated *m*-cresol with propene in the presence of hydrofluoric acid. In spite of the low temperature at which the reaction was carried out (0°–20°), he separated monoisopropyl-*m*-cresol. In the presence of the same catalyst, s-hexylresorcinol and s-hexyl-α-naphthol were prepared from 3-hexene and the corresponding phenols in yields of 45–57%.[100] A number of patents[101-105] describe the use of hydrogen halides in the alkylation of phenols by alkenes.

In the literature there are scattered references to the use of other halogen compounds in this reaction — in particular perchloric acid[104], its salts[105-106], and phosphorus oxychloride[107,108]. Thus, in the presence of a mixture of the perchlorates of aluminium and iron, or of lead perchlorate, *o*-cresol is alkylated by octene and decene with the formation of 4-s-octyl- and 4-s-decyl-*o*-cresols respectively[106]. Thus, a catalyst of this type favours the preparation of mainly *p*-isomers.

The use of phosphorus oxychloride[107,108] in the alkylation of phenol by isobutene makes it possible to obtain the *o*-isomer in considerably greater quantity than the *p*-isomer. It has been established that the temperature exerts an insignificant influence on the ratio of the isomers[107].

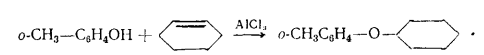
2. Catalytic Action of Metal Chlorides in the Alkylation of Phenols by Alkenes

It has been found that aluminium chloride can be used without activators in the alkylation of phenols by alkenes, giving high yields of alkylphenols. The mode of action of the aluminium chloride in this case, as of other catalysts with an electron deficit in the molecule, leads to the formation of an activated complex with the alkenes:



This complex interacts with the electron pair of the aromatic nucleus, after which the catalyst is eliminated[109].

As in the use of sulphuric acid, the reaction is accompanied by the isomerisation of the radical, and also by its rupture, for example on introduction of the t-octyl radical into the nucleus. Smith[110], by the alkylation of phenol with diisobutene in the presence of aluminium chloride obtained a 67% yield of t-butylphenol and only 14% t-octylphenol. A side reaction in the alkylation with alkenes in the presence of aluminium chloride is the formation of chloro derivatives[111], by the addition of hydrogen chloride to the initial alkene, which the low temperature favours[112]. The formation of alkylphenyl ether or of alkylphenols in the alkylation of phenols by alkenes in the presence of aluminium chloride is determined by the reaction temperature. Nortz[111] carried out the reaction between *o*-cresol and cyclohexene at 30° and obtained the corresponding cyclohexyl ether:



Levas[112] suggested two different ways of carrying out this reaction to yield as the final product the alkoxybenzene or the alkylphenols: (1) formation of the ether by carrying out the reaction in carbon disulphide at 0° and (2) synthesis of the alkylphenols at 100° without a solvent. In this reaction cyclohexene and other cyclic unsaturated hydrocarbons have been used, for example, terpenes[113]. Thus, from 2,4-dialkylphenols, 2,4-dimethyl-6-isobornylphenol and 2,4-di-s-butyl-6-isobornylphenol were prepared. The size of the alkyl groups in the starting phenol is limited to five carbon atoms on account of steric hindrance.

In recent years, aluminium chloride has come into use in this reaction in the form of a compound with sulphuric acid, to which authors give the formula $AlCl_2 . HSO_4$.[114] The preparation of detergents based on alkylphenols with a long chain of carbon atoms, synthesised in the presence of this catalyst, by the alkylation of phenol at 80° with alkene polymers containing from 16 to 30 carbon atoms has

been described[114]. In certain cases, a little boric acid is added to the aluminium chloride[115].

Zinc chloride has also been used as catalyst for the alkylation of phenols by alkenes. A series of patents[116-119] describe the use of zinc oxide and gaseous hydrogen chloride for this purpose.

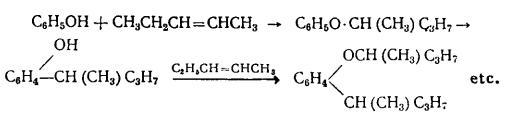
Shuikin and coworkers[120] used a mixed catalyst of zinc chloride and aluminium oxide for the alkylation of the isomeric cresols by pentenes. The reaction was carried out at 150° and 2–3 atm, and in all cases was accompanied by the isomerisation of the initial alkene; the final product of alkylation of the cresols by normal pentenes was s-pentylcresol and that in the alkylation by isopentenes consisted of t-pentylcresols, mainly the *o*-isomers[63,120].

The literature refers to the use in this reaction of ferric chloride[113,121] and stannic chloride[113,122]. Aluminium silicates have also been used in the production of alkylphenols. The reaction is carried out by mixing the initial phenol, alkene, and an inert diluent (cyclohexane or low-boiling paraffin), and passing the mixture over the catalyst at 90°–200° under 6–60 atm pressure[123]. In certain cases the catalyst is placed in a vertical tube into the bottom of which the alkene (isobutene) is let in, and the phenol is added from above. In this way, at 127° and 15 atm, 2,4-di-t-butylphenol (yield 48%) and other alkylphenols were obtained[124]. Where a higher-boiling alkene (diisobutene) was used, the reaction with the aluminium silicate catalyst is carried out at atmospheric pressure[125]. The use of activated silicates as alkylation catalysts is also described in other American patents[126-128].

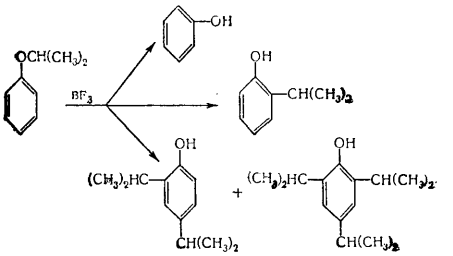
3. Boron Fluoride as Catalyst for the Alkylation of Phenols by Alkenes

During recent years boron fluoride has become widely used as an alkylation catalyst, and various other catalysts based on it have been prepared*.

A series of molecular compounds of boron fluoride, $(C_2H_5)_2O.BF_3$, $H_3PO_4.BF_3$, $BF_3.H_2O$, etc.[130-132] are used as catalysts in the alkylation of phenols by alkenes. Boron fluoride as a catalyst possesses one clearly marked peculiarity, namely the power of polymerising alkenes at a relatively low temperature. Thus in its presence propene polymerises to products above the trimer even at ordinary temperature. Therefore, in the utilisation of boron fluoride for the alkylation of phenols, careful choice of the catalyst concentration, temperature, and time of contact is required. As in the use of other catalysts, in working with boron fluoride either alkylphenols or the phenolic ethers may be formed. Sova[133] obtained a mixture of *o*-isopropylphenol and phenyl isopropyl ether on alkylation of phenol by propene in the presence of boron fluoride at -2°. Zavgorodnii[134] showed that the reaction of phenol with 2-butene between -10° and -5° gives s-butylphenol, which amounts only to one-third of the total quantity of the reaction products formed in a yield of 81%. At room temperature the total yield reaches 90%, through an increase of the quantity of alkylphenols in the catalysate. On further increase of temperature to 53° monoalkyl derivatives of s-butyl phenyl ether are formed. The reaction of phenol with 2-pentene goes similarly[135]:



As in the alkylation of phenols by alkenes in the presence of sulphuric acid, it seems that in alkylation with boron fluoride the reaction goes through the formation of a phenolic ether which subsequently isomerises to a second intermediate possessing a quinonoid structure[136]. Such an isomerisation in the presence of boron fluoride is accompanied by the formation of the phenol and also of the di- and tri-substituted phenols and the corresponding ethers[137], which considerably complicates the separation of the alkylation products:



In the patent literature[138] it is stated that the use of $BF_3-H_3PO_4$ makes possible the preparation of monoalkyl phenols. The use of a large excess of phenol (2–6 moles per mole of alkene) in the presence of this catalyst gave *p*-t-butylphenol in 80% yield. By a similar method *p*-isopropylphenol, t-butyl-*m*-cresol and cyclohexylphenol were prepared.

Another peculiarity of the boron fluoride-phosphoric acid catalyst is its power of directing the entering alkyl group to the *p*-position, while in the majority of cases, when boron fluoride is used, the *o*-isomer preponderates in the alkylation products[133,139]. The alkylation of phenols by alkenes in the presence of boron fluoride is described in a series of patents. The temperature recommended for this reaction varies within wide limits from 25°[140] to 100°[141-143], and the quantity of catalyst amounts to 0.1–1.5 wt.% of the phenol taken[143-145].

In view of the possibility of the polymerisation of the alkenes by boron fluoride, the alkylation of phenols by alkenes is sometimes carried out by first polymerising the alkene and allowing the polymer to alkylate the phenol. This gives the possibility of preparing alkylphenols with long side chains; these find wide application for the preparation of emulsifiers and detergents[146-150]. However, in those cases where polymerisation of the initial alkene is not desired, a large excess of phenol (1 : 6) must be used[138].

High yields of alkylphenol can be obtained by the use of boron fluoride etherate as catalyst. Topchiev and coworkers[130,151] prepared alkylphenols in this way in almost quantitative yields, mostly *p*-substituted. Thus, the molecular compound of ether and boron fluoride produces the same orientation of the substituent as does the molecular compound of boron fluoride and phosphoric acid[138]. Apart from open-chain alkenes, cyclic olefines have also been used in the synthesis of alkylphenols in the presence of boron fluoride. Lefebvre and Levas[152] investigated in detail the reaction of cyclohexene and phenol in the presence of boron fluoride. On carrying out the reaction at 0°, phenoxycyclohexane was obtained in a yield of 61%, with

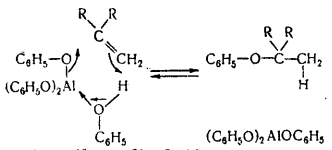
* For the properties of boron fluoride and its application in alkylation, see Topchiev et al.[129].

only 14% of cyclohexylphenol, of which 80% was the *o*-isomer and 20% the *p*-isomer. Under other conditions, at 19°–36° in carbon disulphide, the yield of cyclohexylphenols reached 57% (76% of *p*-isomer and 24% of *o*-isomer)[153]. The di- and tri-alkyl derivatives, together with the mono-alkyl derivatives, were formed[154]. From *o*-cresol, under the same conditions, 2-methyl-4-cyclohexyl and 2-methyl-6-cyclohexylphenols were prepared in a yield of 54%, together with 41% of *o*-methylphenoxycyclohexane[155]. Besides cyclohexene, certain terpenes have been used in this reaction: menthene[156], dipentene*[157], terpinolene[113,157], pinene and limonene*[158].

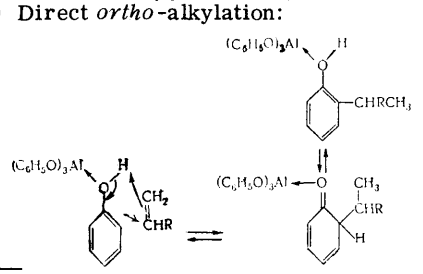
Apart from the acid catalysts described above, certain metallic salts and oxides are employed in the alkylation reaction. Thus, by alkylating phenol with ethylene in the presence of basic aluminium phosphate at 280°–400° and 40–100 atm, Semerano[159] prepared ethyl- and diethyl-phenols. Under approximately the same conditions, Shaad prepared *o*-isopropylphenol[160] using calcium hydrogen phosphate as catalyst. In the literature there is a mention of the use of other salts — molybdates of copper, nickel, and cobalt[161].

Particular interest attaches to the use of aluminium phenoxide as catalyst for the alkylation of phenols by alkenes to prepare the inaccessible *o*-substituted alkylphenols. This has been described in a series of papers in recent years. As is well known, the *p*-derivative usually preponderates in alkylation reactions; consequently, if the *p*-position is not blocked the 2,6-dialkylphenols are not formed and their synthesis must be brought about indirectly. The use of this catalyst in the synthesis of a series of *o*-alkyl- and *o,o'*-dialkyl-phenols by the alkylation of phenol with alkenes has been described by Kolka[162,163]. As in other cases, the nature of the final product depends on the temperature: at a relatively low temperature the phenolic ether is formed, while at a higher temperature the *p*-isomer is obtained; thus, aluminium phenoxide can serve for the *ortho*-alkylation only within a definite temperature range. Kolka established that the reactivity of the alkenes falls in the series $R_2C=CH_2 > RCH=CH_2$ or $RCH=CHR > CH_2=CH_2$, which is typical of reactions involving the formation of a carbonium ion. As is known, aluminium alcoholates form coordination compounds with the alcohol, and although acids of the type $HAl(OR)_4$ have not been isolated, some authors[162,163] postulate their existence and suggest the following mechanism for this reaction.

(*a*) Ether formation:

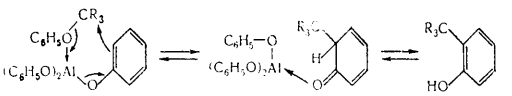


(*b*) Direct *ortho*-alkylation:



* Dipentene and limonene are the same compound (Ed. of Translation).

(*c*) *Ortho*-alkylation through the ether:



Under the optimal conditions found for each case, the corresponding 2-alkyl- and 2,6-dialkyl-derivatives were prepared in high yields: 2,6-di-s-butylphenol (74%), 2-cyclohexylphenol (42%), 2-(dec-2-yl)phenol (49%), 2,6-diisopropylphenol (61%), 2-ethyl-6-s-butylphenol (58%).

Stroh[164] has obtained similar results. The preparation of a series of *o,o* -disubstituted phenols by the alkylation of phenol with ethylene, propene, isobutene, etc., in the presence of the above catalyst has been described in a U.S. patent[165]. A number of patents[166,167] have described the alkylation of phenol, ethylphenol, and cresol by alkenes in the presence of metals that form salts with the phenol (aluminium, zinc, etc.). To increase the rate of solution of aluminium in the phenol, the addition of mercuric chloride is recommended[168].

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A survey of the results in the literature on the catalytic alkylation of phenols by unsaturated hydrocarbons shows that the most widely used catalyst is sulphuric acid. The high yields of alkylphenols and the accessibility of sulphuric acid give a certain advantage compared to the other catalysts used in this reaction. If the structure of the original phenol permits, alkylation in the presence of sulphuric acid usually forms a mixture of *o*- and *p*-alkylphenols, in which a rise of temperature leads to an increase in the yield of the *p*-isomer. Apparently, alkylation in the presence of ion-exchange resins is quite promising, and leads to high yields of alkylphenol and not to rupture of highly branched alkenes (of the diisobutene type), as occurs when sulphuric acid and aluminium chloride are used. The use of boron fluoride and of a few of its molecular compounds is very interesting in those cases where the alkylation may be combined with a preliminary polymerisation of the original alkene in order to prepare alkylphenols with long side chains — initial substances in the synthesis of detergents. However, here much work is still required in the investigation of the conditions necessary for the preparation of a particular product.

For the synthesis of *o*-alkylphenols it is apparently necessary to employ aluminium phenoxide; within a definite temperature interval it is then possible to obtain high yields of *o*-alkylphenols, which are not easily accessible.

II. ALKYLATION OF PHENOLS BY ALCOHOLS*

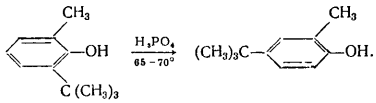
In the synthesis of alkylphenols by the catalytic alkylation of phenols with alcohols, a much smaller number of

* Apart from alcohols, the corresponding ethers or sulphonic acid esters may be used as alkylating agents[168]. It seems that the ethers, under the influence of the catalyst, break down with formation of a carbonium ion, which takes part in the electrophilic substitution reaction of the aromatic nucleus being alkylated[169]. Ethyl *p*-toluenesulphonate[170], benzyl benzenesulphonate[171] and diisopropyl sulphate[172] have been used as alkylating agents.

catalysts has been used to carry out the reaction in the liquid phase; the chief are phosphoric acid, chlorides of aluminium and zinc, and, to a less extent, sulphuric acid and boron fluoride. For alkylation in the vapour phase, aluminium oxide and natural clays are used as catalysts.

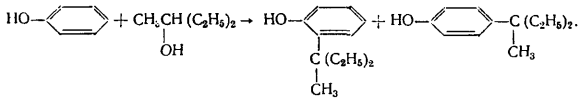
Phosphoric acid is preferred to other catalysts in the alkylation of phenols, because, by using equimolar quantities of the reacting substances, it is possible to prepare monoalkylphenols in yields up to 90%; with other catalysts, complicated mixtures of various alkylation products are formed.

Tsukervanik and Tambovtseva[173] investigated the temperature conditions for the alkylation of phenols by various alcohols in the presence of phosphoric acid. They established that the condensation goes on only at a raised temperature: tertiary alcohols react between 70° and 80°, iso-alcohols [primary and secondary iso-alcohols? (Ed. of Translation)] enter into reaction at 80°–100°, and for alkylation by normal primary alcohols the temperature required reaches 100°–130°. In the alkylation of phenols by alcohols at these temperatures, mainly the *p*-isomers are formed. The highest yields of alkylphenols are obtained in the alkylation with tertiary and secondary alcohols. Chichibabin[174] showed that among primary alcohols only benzyl alcohol reacts well. In a series of papers[174-177] he confirmed that secondary and tertiary alcohols condense with phenols at 50°–65°, forming mainly *o*-alkylphenols, with little *p*-isomer. Hart[178] later showed, by carefully investigating the products of alkylation of *m*-cresol by trimethylcarbinol under the conditions used by Chichibabin, that the tertiary butyl group enters the position *ortho* to the hydroxyl and *para* to the methyl group. However, Chichibabin's statement that he prepared 2-methyl-6-t-butylphenol by the alkylation of *o*-cresol with trimethylcarbinol is incorrect, since the substituted phenol prepared by him was easily soluble in 10% alkali, which is not the case for *o,o*-disubstituted phenols. Hart[178] synthesised 2-methyl-6-t-butylphenol by another method and it differed from the compound previously prepared by Chichibabin. Therefore, the latter substance probably consisted of the *p*-isomer formed from the corresponding *o*-isomer as a result of the isomerising influence of the temperature and phosphoric acid. This was confirmed by Hart in an experiment on the isomerisation of 2-methyl-6-t-butylphenol:

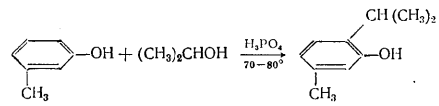


Under the same conditions, 4-t-butyl-*o*-cresol was also prepared by Dubinin[179]. Thus, as in the presence of certain other catalysts, the position taken by the radical to a large extent depends on the structure of the initial phenol and on the temperature.

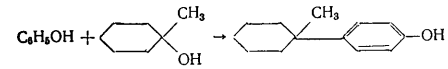
Buu-Hoï[180], in the alkylation of phenol by methyldiethyl carbinol in the presence of phosphoric acid, prepared *o*- and *p*-t-hexylphenols:



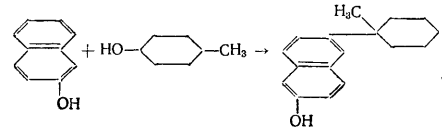
Mitsui[181] synthesised 2-methyl-4-isopropylphenol by the condensation of *o*-cresol with isopropyl alcohol. Several workers have investigated the alkylation of dihydric phenols by aliphatic alcohols in the presence of phosphoric acid. Thus, Tambovtseva[182] prepared the corresponding alkylresorcinols and alkylcatechols in yields up to 70% by the alkylation with isopropyl and n-butyl alcohols. The optimal temperature for the alkylation with isopropanol was 120°–140° and for the reaction with n-butanol it was 150°–160°. Buu-Hoï[183] prepared 4-t-pentylresorcinol, 4-t-butylguaiacol, and 4-t-butylcatechol by the alkylation of the corresponding phenols with isopentyl and isobutyl alcohols. The alkylation of *m*-cresol by isopropyl alcohol is described in the patent literature for the preparation of thymol[184]:



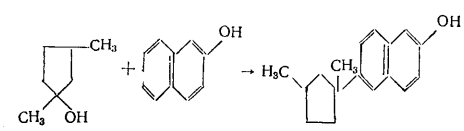
The use of cyclic alcohols in this reaction gives high yields of cyclohexylphenols. Thus, Abdurasuleva[185] prepared a mixture of *p*-cyclohexylphenols in 80% yield by the alkylation of phenol with cyclohexanol. Sidorova[186] isolated 4-(1-methylcyclohexyl)phenol from the products of the alkylation of phenol with 1-methylcyclohexanol at 100°–120°, the *o*-isomer not being found in the reaction products:



It is interesting that even at the relatively high temperature employed an ether was also formed and, in the process of distillation, was transformed into 4-(1-methylcyclohexyl)phenol, the total yield of which finally amounted to 79%. Cyclohexanol was used for the alkylation of β-naphthol[183] under the conditions suggested by Chichibabin[177]; the yield of 6-cyclohexyl-2-naphthol formed in this way was, however, very small. The authors proved the structure of this isomer by a series of reactions. It was suggested that its formation resulted from an increased electron density in positions 1 and 6 of the naphthalene[187]. The alkylation of β-naphthol by methylcyclohexanols gives good yields of the monosubstituted product, the structure of which is identical for all three isomers; for example, in the case of 4-methylcyclohexanol the reaction goes in the following way:



Thus, apparently, an isomerisation of the methylcyclohexenes formed as intermediates takes place. This phenomenon was earlier observed by Schrauth[36], who, in the alkylation of phenol by isomeric methylcyclohexanols in the presence of sulphuric acid, obtained in all cases one product, namely 4-(1-methylcyclohexyl)phenol. Buu-Hoï[188] used 1,3-dimethylcyclopentanol in this reaction and obtained 6-(1,3-dimethylcyclopentyl)-2-naphthol:



The quantity of phosphoric acid necessary for the reaction is very large. Thus, in the preparation of monoalkylphenols, 400 g of phosphoric acid are required per mole of phenol and per mole of alcohol[174,176,177]. For the introduction of two or three alkyl groups into the phenol nucleus, a correspondingly increased quantity of alcohol is used with the same quantity of phosphoric acid[189]. By the alkylation of phenol with n-butyl alcohol at 130°–150°, Sidorova[189] prepared dibutylphenol in 70% yield. The yield of the trisubstituted derivatives at this temperature is not high, apparently because under these conditions partial dealkylation takes place.

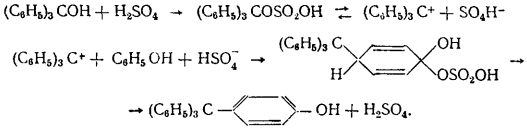
The use of sulphuric acid in the alkylation of phenols by alcohols has been described in only a few publications, mainly patents. Aliphatic alcohols*, cyclohexanol, and certain aromatic alcohols have been employed. The alkylation of phenol by aliphatic alcohols was carried out at 10°–25°[191-192], and also at higher temperatures, from 90° to 160°[193,194]. Thymol[194], *o*-s-butylphenol[195], t-butylphenol, and t-pentylphenol[196,197] were prepared from *m*-cresol, phenol, and the respective aliphatic alcohols. There is a very interesting paper by Meyer and Bernhauer[198], who investigated the alkylation of phenols by alcohols in the presence of 70% sulphuric acid. It was found that the reaction goes at 70°–80° with any aliphatic alcohol, and with benzyl alcohol, even at 40°. The authors suggest that the reaction proceeds via the formation of the corresponding unsaturated hydrocarbons with their subsequent transformation to alkylsulphonic acids, which then alkylate the aromatic nucleus. This, the authors suggest, explains the impossibility of carrying out the reaction with methyl alcohol. However, the mechanism of alkylation by benzyl alcohol and the unusual ease with which it condenses remain unclear. Deno and Chafetz[199] carried out the alkylation of hydroquinone at 0°–5° in the presence of 75–90% sulphuric acid. They isolated disubstituted hydroquinones in yields of 40–70%. In some papers it is indicated that, for increased yields, the water formed must be removed. One of the patents[200] describes the alkylation of phenols by isobutyl and isopentyl alcohols in the presence of sulphuric acid in such a way that the water formed is removed; the yield of alkylphenol exceeds 90%. The alkylation by cyclohexanol[201] proceeds similarly.

In alkylation in the presence of sulphuric acid, isomerisation of the substituting radical is always observed, which suggests that isomerisation occurs in the alkyl cation formed in the reaction between the alcohol and the sulphuric acid:

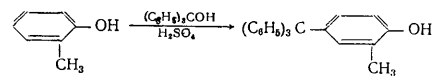
$$CH_3CH_2CH_2OH + HOSO_3H \rightarrow [CH_3CH_2\overset{H}{\overset{\vdots}{C}}H_2OH]^+ + (OSO_3H)^-$$
$$(OSO_3H)^- + H_2O + CH_3\overset{+}{C}HCH_3 \leftarrow CH_3CH_2CH_2^+ + H_2O + (OSO_3H)^-$$

Of the aromatic alcohols, benzyl alcohol[198,202,203] and triphenylcarbinol[204-207] have been used for the alkylation of phenols. The latter has been employed with a Baeyer's technique[205]; the reaction was carried out in the presence of a mixture of sulphuric and acetic acids. In this, the yield of, for example, 4-hydroxytetraphenylmethane reached 97%. The authors[204] suggest that the reaction goes through the intermediate formation of a carbonium ion as follows:

$$(C_6H_5)_3COH + H_2SO_4 \rightarrow (C_6H_5)_3COSO_2OH \rightleftarrows (C_6H_5)_3C^+ + SO_4H^-$$



Alkylation of *o*- and *m*-cresols under similar circumstances gives high yields (up to 80%) of the corresponding substituted tetraphenylmethane, for example:

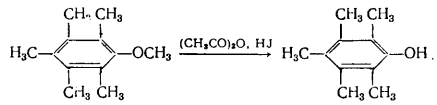


The use of anhydrous hydrogen fluoride in this reaction is very interesting. Calcott[99] described the alkylation of certain phenols in the presence of this catalyst at 2°–25°. The alkylation proceeds smoothly, without side reactions; it is always the nucleus that is alkylated and not the oxygen, because the other does not isomerise under the reaction conditions. Triisopropylphenol (94% yield), monoisopropylhydroquinone (39%), diisopropyl-2-naphthol (94%), etc. were prepared[99]. As with the alkenes, perchloric acid is sometimes used in alkylation by alcohols[208,209].

Investigations of the use of boron fluoride in the alkylation of phenols are described in only a few papers. Thus, Sowa[210] showed that neither methyl nor ethyl alcohol react with phenol in the presence of boron fluoride on heating at atmospheric pressure; they react at 170° in a sealed tube, in which the main product consists of alkyl phenyl ethers, alkylphenols being formed in only small quantity. At 115° n-propyl and isopropyl alcohols give an identical product — the isopropyl ether of *O*-isopropyl-2,4-diisopropylphenol. The authors consider that this proves that the reaction involves the intermediate formation of an alkene as follows:

$$C_nH_{2n+1}OH \rightarrow C_nH_{2n} + H_2O,$$
$$C_6H_5OH + C_nH_{2n} \rightarrow C_6H_5OC_nH_{2n+1},$$

and not the initial formation of an ether and its subsequent rearrangement. The methylation of the phenol nucleus in the presence of boron fluoride was achieved by Kolka and Vogt[211]: methyl alcohol was saturated with boron fluoride to give boron fluoride etherate, $(CH_3)_2O.BF_3$, which on boiling with phenol formed methyl ether and the *O*-methyl derivatives of the phenols. The latter are easily converted to the corresponding phenols by hydriodic acid:



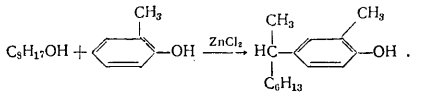
Apart from boron fluoride, the use of fluoroboric acid[212] has been described, but it possesses no advantage over sulphuric acid for alkylation with alcohols.

Metal chlorides have been used for a long time in the alkylation of phenols by alcohols. Liebmann[213,214] showed that the reaction goes very easily on short heating of the reactants at 180° in the presence of zinc chloride. Senkowski[215] later showed that the phenols prepared by Liebmann consisted of the *p*-isomers. Later still Anschütz[216] discovered that in the presence of zinc chloride an isomerisation occurs, so that the phenols prepared by Liebmann were t-alkyl derivatives. The technique suggested by

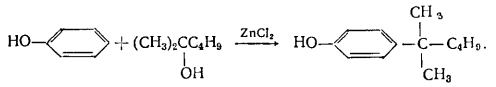
* In a Japanese patent[190], the alkylation of phenols by ethers, for example, di-n-butyl ether, in the presence of sulphuric and other acids, is described.

Liebmann was later utilised in the alkylation of phenol by n-butyl[217], s-butyl[218], t-pentyl[219], dodecyl[220], and cetyl[221] alcohols, by cyclohexanol[218], and also in the alkylation of the cresols by isobutyl alcohol[222,223] and of guaiacol by various alcohols[224].

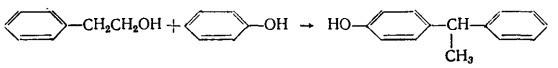
Degering[225] observed that the alkylation of phenols in the presence of zinc chloride usually occurs in the *p*-position, and when this is substituted, in the *o*-position, without the formation of *m*-isomers, in contrast to the case when aluminium chloride is used. The author carried out the alkylation of *o*-cresol by octyl, dodecyl, caprilic, and other alcohols and found that in the mixture of isomers formed the 2-methyl-4-alkylphenol predominated, for example:



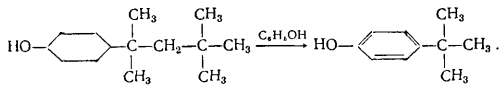
In the alkylation of *p*-cresol the corresponding *o*-alkyl-*p*-cresol is formed, the yields reaching 70%. The formation of the *p*-isomers was also observed by McGreal[80] in the alkylation of phenol by dimethylisopropylcarbinol and dimethyl-n-butylcarbinol in the presence of zinc chloride:



Diisobutyl alcohol (2,2,4-trimethylpentan-4-ol) does not form *p*-t-octylphenol with phenol under analogous conditions, the chief reaction product being *p*-t-butylphenol. The author[81] investigated the behaviour of primary, secondary, and tertiary aromatic alcohols in this reaction: phenylcarbinol, phenylmethylcarbinol, benzylcarbinol, phenylmethylethylcarbinol, and phenylmethylisopropylcarbinol. When benzylcarbinol was used, instead of the expected 4-hydroxydibenzyl, *p*-(α-phenylethyl)phenol was isolated:



The formation of such a phenol indicates that dehydration of the alcohol precedes the reaction with the phenol. In the case of the remaining carbinols the condensation went normally with the formation of the corresponding *p*-alkylphenols, the yields of which varied from 40 to 80%. Cyclic alcohols (cyclohexanol and cyclopentanol) alkylate phenol at 170°–180°, in the presence of zinc chloride, giving a mixture of *o*- and *p*-substituted phenols[226]. The isomeric methylcyclohexanols form methylcyclohexylphenol[80] in this reaction. An attempt to introduce 4-t-octylcyclohexanol into the reaction with phenol under similar conditions did not yield the desired result, as *p*-t-butylphenol was again obtained:



The alkylation of phenol by primary alcohols in the presence of zinc chloride in hydrochloric acid solution at 100°–140° has been described[227,228]. For example, *p*-t-butylphenol was thus prepared[228]. There is also mention of the use in this reaction of magnesium chloride[229]; reaction of *m*-cresol with propyl alcohol in a sealed tube at 200°–210° gave methylpropylphenol. Recently magnesium chloride has not been used, apparently on account of its greater cost and the difficulty of its regeneration.

The use of aluminium chloride in the alkylation of aromatic compounds by alcohols has been investigated in detail by Huston, Tsukervanik, and others. In the early papers the view is expressed that primary alcohols do not enter the condensation reaction in the presence of aluminium chloride, and that secondary alcohols condense with difficulty. Huston[230], for example, considered that condensation was possible only with alcohols in whose molecules the hydroxyl was activated by a double bond or a benzene ring. Later, Tsukervanik[231] showed that for the condensation of phenols with primary and secondary alcohols, different proportions of the reagents and a higher temperature were required. Huston[230] conducted his experiments at 25°–30° with molar proportions of phenol, alcohol, and aluminium chloride of 1 : 1 : 0.5. Tsukervanik[231], using a different proportion, 1 : 1 : 2*, and a higher temperature (110°–125°), obtained up to 70% of mixtures of the *o*- and *p*-isomers in the alkylation of phenol by ethyl, propyl, n-butyl, isobutyl, and isopentyl alcohols. The reaction between phenol and secondary alcohols (isopropyl, s-butyl, and s-pentyl) in the presence of aluminium chloride gave the corresponding alkylphenols (up to 52%). Together with the alkylphenols, alkyl phenyl ethers were also found as reaction products, in quantities increasing with decreasing amount of catalyst and lowering of temperature. Therefore, Tsukervanik[231] suggested that alcoholates of the primary and secondary alcohols are first formed, and later react further:

$$ROH + AlCl_3 \rightarrow ROAlCl_2 + HCl\ ,$$
$$C_6H_5OH + AlCl_3 \rightarrow C_6H_5OAlCl_2 + HCl\ ,$$
$$C_6H_5OAlCl_2 + ROAlCl_2 \xrightarrow{HCl} C_6H_5OR + AlCl_3 + AlCl_2OH,$$
$$C_6H_5OR + ROH + AlCl_3 \rightarrow RC_6H_4OR + AlCl_2(OH) + HCl.$$

In the further decomposition of the alkyl phenyl ether three possibilities may be envisaged:

$$RC_6H_4OR + HCl \rightarrow RC_6H_4OH + RCl\ , \quad (I)$$
$$RC_6H_4OR + C_6H_5OH \rightarrow 2RC_6H_4OH\ , \quad (II)$$
$$2RC_6H_4OR \rightarrow RC_6H_4OH + R_2C_6H_3OR. \quad (III)$$

The possibility of reaction (I)[233], and reactions (II) and (III)[234,235] was confirmed. Subsequently, the possibility of the formation of mixed alcoholates of aluminium was assumed by many investigators[236,237], who suggested that these compounds decompose as follows:

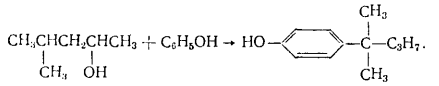
$$AlCl_2OR \rightarrow RCl + AlOCl.$$

This reaction may be utilised for the synthesis of alkyl halides. However, Tsukervanik[238] considers that a process of this nature requires a higher temperature (140°–150°), while the alkylation of phenol takes place at 90°–100°, and that at the temperature of maximum decomposition of the mixed alcoholates, the yields of alkylated products are not raised, but are actually lowered. The decomposition of the ethers thus apparently takes place through stage (II) or (III).

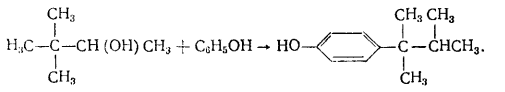
More recently, Huston[239] has achieved the condensation of phenol with more complicated secondary alcohols. The alkylation of phenol by 2-pentanol and 3-pentanol and also

* With smaller quantities of aluminium chloride, the yields did not exceed 36%.[232]

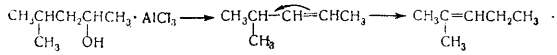
by 2-hexanol and 3-hexanol, etc. was carried out under the conditions described above[230]. The nature of the products obtained depends on the structure of the initial alcohol. Thus, the alkylation of phenol by 2-pentanol and 3-pentanol gives 2-(*p*-hydroxyphenyl)pentane and 3-(*p*-hydroxyphenyl)-pentane, and the alkylation of phenol by 2-methylpentan-4--ol gives 2-methyl-2-(*p*-hydroxyphenyl)pentane as chief product:



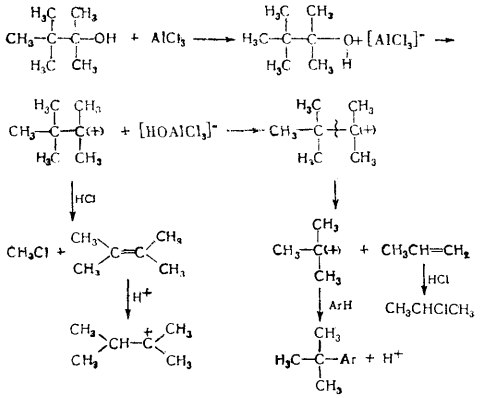
This reaction proceeds with the isomerisation of the substituting radical. Alkylation of phenol by 2,2-dimethylbutan-3-ol yields 2,3-dimethyl-2-(*p*-hydroxyphenyl)-butane:



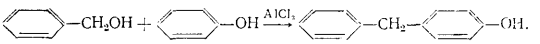
Huston and coworkers[239] suggested a mechanism for the alkylation of phenols by secondary alcohols, different from that described above. According to their ideas, aluminium chloride forms with secondary alcohols a complex that easily breaks down directly, or through the aluminate, with the formation of an alkene; this condenses with phenol in the presence of aluminium chloride. The authors consider that this explains the formation of 2-methyl-2-(*p*-hydroxyphenyl)pentane in the alkylation of phenol by 2-methylpentan-4-ol, if a migration of the double bond is supposed to precede the condensation:



The formation of 2,3-dimethyl-2-(*p*-hydroxyphenyl)-butane is explained by Huston and coworkers[239] by the appearance of an unstable carbonium ion $(CH_3)_3C-\overset{+}{C}HCH_3$, which rearranges to a more stable ion $CH_3\overset{+}{C}(CH_3)-CH(CH_3)_2$; this then condenses with the phenol. The alkylation of phenol by tertiary alcohols has been described in a series of other papers[240-247]; the yields of alkylphenols obtained varied from 2 to 80%. Huston[248,249] explains the low yields of *p*-t-alkylphenols and the formation of side products in the alkylation with alcohols having a branched chain, by the occurrence, during the alkylation in the presence of aluminium chloride, of side reactions. For example, the alkylation of benzene by 2,3,3-trimethylbutan-2-ol goes according to the scheme



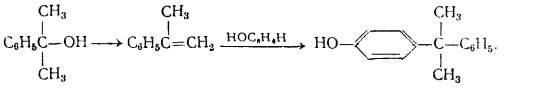
Such products have been found in the alkylation of phenols by branched-chain alcohols[245], which suggests that reactions similar to the above may also be involved. The alkylation of phenols by aromatic alcohols goes easily. Benzyl alcohol reacts with phenol in petrol ether solution at 45°–60° with the formation of up to 45% of *p*-benzylphenol[250]:



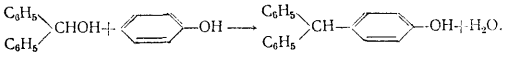
At a lower temperature (35°) the reaction hardly occurs at all. The isomeric cresols are benzylated even at 30°–35°, forming a mixture of mono- and di-substituted derivatives[251-253]. Secondary aromatic alcohols condense with phenol at temperatures of the order of 25°–40°; for example, benzohydrol gives with phenol up to 40% of *p*-hydroxytriphenylmethane:

$$(C_6H_5)_2CHOH + C_6H_5OH \rightarrow (C_6H_5)_2CHC_6H_4OH.$$

This reaction goes particularly easily with alcohols containing one or more phenyl radicals in the molecule[254-256]. With increase of the number of phenyl radicals, the yield of substituted phenols rises[255]. Thus, in the condensation of phenol with dimethylphenyl-, methyldiphenyl-, and triphenyl-carbinol the yield of *p*-substituted products amounted to 72, 80, and 95% respectively[255]. In the first two cases, an alkene was found in the reaction mixture — a product of the dehydration of the original carbinol. Welsh[255], therefore, supposes that the alkylation goes as follows:



The possibility of such a reaction mechanism when zinc chloride is used, was confirmed by McGreal[80]. In those cases where the formation of a phenylalkene is impossible, it is suggested that the water is formed from a hydrogen of the nucleus and the hydroxyl of the alcohol:



Tsukervanik and Nazarova[257] used ferric chloride in this reaction. It transpired that tertiary alcohols react with phenol and the cresols, even at room temperature, forming monoalkyl derivatives in a yield of 70–95%. The quantity of ferric chloride amounted to 0.5 g-equiv. to 1 g-equiv. of alcohol. In the alkylation by secondary alcohols 1 g-equiv. of ferric chloride was required for the same quantity of alcohol, and a temperature to 50°–60° was necessary; the yield of alkylphenols reached 38–75%. The success of this reaction with primary alcohols depends on the structure of the original alcohol. With iso-alcohols, the reaction goes at a higher temperature (120°), but normal alcohols do not condense with aromatic compounds in the presence of ferric chloride[258].

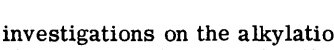
The alkylation of phenols by alcohols at a high temperature is carried out with aluminium oxide, natural clays, and aluminium silicates as catalysts. Ipat'ev and coworkers[259-261] brought about the alkylation of phenol by methyl alcohol, using aluminium oxide as catalyst at 440° and 220 atm pressure. The use of the high pressure made it possible to prepare *o*-cresol, since in the absence of

this pressure, only hexamethylbenzene is formed[262]. Ethyl alcohol gives a smaller yield[263]. Alkylation by propyl alcohol[263] was carried out at 400° and 130 atm; *o*-propylphenol was found in the alkylate, together with other alkylation products. Cullinane[264] has shown that the composition of the latter depends not only on the conditions of the reaction, but also on the nature of the catalyst used. Thus, if the reaction between methyl alcohol and phenol is carried out at 200°, mainly anisole is formed; a rise of temperature leads to the formation of *o*-, *m*-, and *p*-methylphenols, the proportions of which change with change of temperature and replacement of the aluminium oxide by aluminosilicate. Samsonova[265] investigated the reaction of phenol and methyl alcohol in the presence of a natural aluminosilicate (gumbrine) and showed that a rise of temperature to 500° makes it possible to prepare alkylphenols in a yield of up to 68%. In the alkylation of phenol by ethyl alcohol[266] the optimal temperature is 350°, at which alkylphenols were prepared in a yield of 94%. Aluminium oxide and natural aluminosilicates have been used as alkylation catalysts also in other investigations[267-274]. Aleksandrova[275] suggested a mixed catalyst consisting of thorium oxide and aluminium oxide for the alkylation of phenols by alcohols in the vapour phase. At 440° up to 60% of acidic products were prepared, constituting a mixture of alkylphenols. Hanch[276] showed later that pure aluminium oxide gives analogous results. Among other catalysts for the alkylation of phenols by alcohol in the vapour phase, a two-component silica–phosphoric acid catalyst has been successfully used[277].

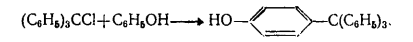
A survey of research on the catalytic alkylation of phenols by alcohols thus shows that the yields of alkylphenol and their structures depend on the conditions of the reaction, among which the structure of the initial alcohol, the temperature, and the nature of the catalyst are determining factors; in some cases, the phase and pressure factor play a significant part. However, in spite of the possibility of preparing in this way alkylphenols in high yields, often reaching 90% and more, the alkylation of phenols by alcohols in industrial practice has only limited prospects, since the results of many investigators show that in the great majority of cases, the alkylation by alcohols proceeds through the formation of the corresponding alkenes. The latter are more accessible and cheaper, since they can be prepared in various processes of refining of petroleum and solid natural fuels (coal, combustible shales, peat, sapropelites). Nevertheless, the catalytic alkylation of phenols by alcohols has a number of advantages in laboratory practice and, therefore, deserves serious attention.

III. ALKYLATION OF PHENOLS BY ALKYL HALIDES

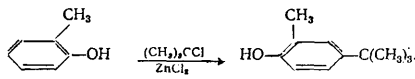
The first investigations on the alkylation of phenols by alkyl halides date back to the second half of the last century. This reaction was investigated by a number of authors, mainly using benzyl chloride. Paterno[278] and then Mazzara[279] and Rennie[280] synthesised benzylphenol by the alkylation of phenol with benzyl chloride in the presence of zinc dust:



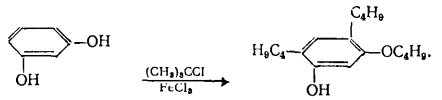
Cresol[281] and anisole[282] were employed in analogous reactions. Triphenylchloromethane also easily enters into a similar reaction, reacting with phenol in the presence of small quantities of copper* with the formation of *p*-hydroxytetraphenylmethane[283,284]:



Later the alkylation of phenols by alkyl halides was achieved mainly using zinc and aluminium chlorides, instead of zinc and copper. Zinc chloride was used by Baur[285] for the synthesis of t-butylcresols, for example:



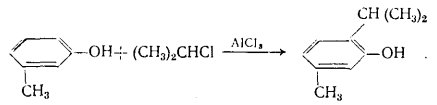
p-Hydroxytetraphenylmethane, 1-(hydroxyphenyl)-2,2,2-triphenylethane[286], and cetylphenol[287] were synthesised in a similar way. The quantity of zinc chloride used, as shown by a number of workers, may be small (0.1–0.2 mole, or even less, per mole of halide[288-290]). The quantity of zinc chloride used by Kuchkarev[288] was only 0.015–0.03 mole per mole of chloride, the zinc chloride being prepared during the reaction, from hydrochloric acid and zinc. In experiments carried out at 180°–200° Kuchkarev[288] prepared up to 70% of s-butylphenols from n-butyl chloride and phenol. An attempt to lower the temperature of alkylation to 100°–150° led to a sharp fall in the yield of alkylphenols[289]. The use of zinc chloride as catalyst in the alkylation of phenol and resorcinol by cyclohexyl chloride gives low yields of cyclohexylphenols, not exceeding 20 and 5%, respectively, of theory[291]. In the alkylation of β-naphthol by tertiary butyl chloride in the presence of zinc chloride, 6-t-butyl-2-naphthol is formed[292,293]; the formation, in this reaction, of 4-t-butyl-2-naphthol described by Contractor[294] is improbable in view of the position of the reactive sites in the naphthalene molecule and the orienting influence of the hydroxyl. In a search for a more active catalyst for the alkylation of phenols, Gurewitsch investigated this reaction in the presence of iron and aluminium chlorides[295], using tertiary alkyl halides, namely t-butyl and t-pentyl chloride and the dihydric phenols resorcinol and catechol. It was found that in the presence of ferric chloride, the ether derived from the alkylphenol is always formed too:



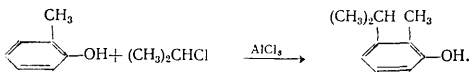
On carrying out the reaction in contact with aluminium chloride, only dibutylresorcinol is formed. Later aluminium chloride came to be fairly widely used in this reaction (described in a series of patents) and ferric chloride was employed in only a few studies[296,297]. The reason for this, apparently, is the formation of mixed products in the ferric chloride reaction, and also the low yields of monoalkylated phenols[298]. The temperature conditions vary within wide limits, according to the structure of the reactants. The alkylation of phenol itself by tertiary alkyl halides usually takes place at a low temperature (up to 50°)[299-303]; there is, however, a mention of this reaction having been carried out under more vigorous conditions (up to 200°)[301]. 4-t-Alkylphenols are usually formed, but small quantities of 2-t- and 2,4,-di-t-alkylphenols[301-304] are also obtained. The preparation of 4-t-butyl-2-naphthol by the alkylation of β-naphthol with t-butyl chloride in the presence of aluminium chloride[302] has been described, but, judging from the paper quoted above[292], formation of 6-t-butyl-2-naphthol apparently also takes place. In the

* Baeyer[283] showed that this reaction goes even in the absence of catalyst.

alkylation of phenol by t-octyl chloride in the presence of aluminium chloride, as with other alkylating agents, formation of *p*-t-butylphenol takes place[305]. Of the secondary alkyl halides, only isopropyl chloride reacts readily; with *m*-cresol (between 0° and 20°), it yields thymol[306]:

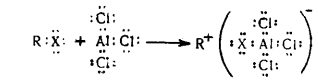


The reaction was carried out in dichloroethane solution. Under similar conditions, *o*-cresol forms 2-methyl-3-isopropylphenol[307,308]:

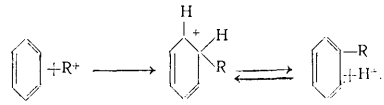


However, alkylation by other secondary and primary alkyl halides is more difficult. Tsukervanik and Tambovtseva[309] alkylated phenol with n-butyl chloride, isobutyl chloride, and isopentyl chloride by heating the mixture of the reactants to 110° in the presence of equimolar quantities* of aluminium chloride. In all cases the alkylphenols and the corresponding alkyl aryl ethers were isolated. On carrying out the reaction at a lower temperature, t-pentylphenol was obtained in a yield of 55%. Benzyl chloride[311] enters into this reaction as easily as tertiary alkyl halides. Hydroxydiphenylmethane[312] is formed in a similar way. It was found that α-halogenated ethylbenzenes react with phenols even in the absence of a catalyst with the formation of di- and tri-(α-phenylethyl)-phenols[313]. α-Phenylethyl chloride reacts with phenol on simply mixing and boiling. Hart[314] used in this reaction an optically active α-phenylethyl chloride, and showed that the alkylation products are formed directly, and not through the phenyl ethers with subsequent rearrangement. He also established that *C*-alkylation in the *p*-position is accompanied by the inversion of the configuration, but in alkylation in the *o*-position the configuration is preserved[315]. Isagulyants and Bagryantseva[316] synthesised *p*-t-butylphenol using t-butyl chloride formed directly in the reaction mixture. For this, they introduced isobutene into the reaction mixture containing phenol in the presence of aluminium chloride and a small quantity of butyl chloride, necessary for starting the reaction. Subsequently butyl chloride is formed from the isobutene and hydrogen chloride is evolved. The yield of alkylphenols reached 64%. The reaction can be carried out even in the absence of butyl chloride, by passing hydrogen chloride into the reaction mixture; in this case the yield of alkylphenols reached 71%. The quantity of catalyst only slightly influenced the yield of alkylphenols. The use of small quantities of alkyl halides as "primers" for the alkylation of phenols by unsaturated hydrocarbons is also described in other papers[317-319].

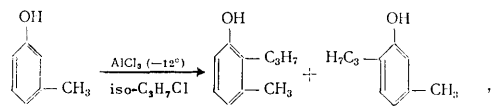
The mechanism of the alkylation of aromatic hydrocarbons by alkyl halides, which has been investigated by many workers, is apparently applicable, in principle, to the alkylation of phenols. Many authors[109,320] explain the reason for the different reactivity of alkyl halides in this reaction, carried out in the presence of aluminium chloride, as follows. It is suggested that the alkyl halide forms an ionic complex with the aluminium chloride:



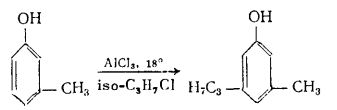
As a consequence of this, there is a weakening of the carbon–halogen bond resulting in the formation of a carbonium ion, and the alkylation itself is one case of electrophilic substitution:



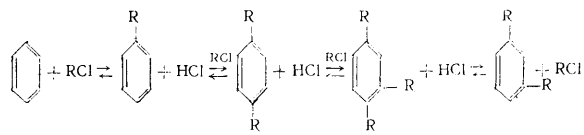
In the tertiary alkyl halides the carbon–halogen bond is extremely weak and, consequently, the formation of a carbonium ion is very probable. In recent times, Brown and coworkers[321] have suggested that the carbonium-ion mechanism cannot explain all cases of alkylation by alkyl halides. The authors regard the carbonium mechanism as applicable only in the case of tertiary alkyl halides and of other easily ionising halogen derivatives; for alkylation by primary alkyl halides they suggest a nucleophilic attack on the aromatic compound by the non-ionised complex formed as a result of reaction of the alkyl halide with aluminium chloride. Secondary alkyl halides react according to the carbonium mechanism; however, by observing special conditions and by using a medium of low dielectric constant, it is possible to achieve a nucleophilic replacement. A very interesting feature of alkylation in the presence of aluminium chloride is the anomalous orientation of the hydroxyl and methyl groups, which usually enter the *o*- and *p*-positions. Chichibabin investigated the preparation of the isomeric thymols by the alkylation of *m*-cresol with isopropyl chloride in the presence of aluminium chloride[322]. He showed that, on carrying out the reaction at -12°, *o*-thymol and 3-methyl-6-isopropylphenol were formed,



and a very insignificant quantity of *m*-thymol. However, at 18° *m*-thymol becomes the chief product of the reaction:



Chichibabin showed that *m*-thymol is the most stable isomer, since the remaining isomers are converted to *m*-thymol on heating with aluminium chloride. He also observed the formation of the *m*-isomer (3-methyl-5-butylphenol) in the alkylation of *m*-cresol by t-butyl chloride[323]. Many authors explain a similar phenomenon of abnormal replacement in the benzene nucleus by the reversibility of this reaction[321,324,325]:



* The quantity of aluminium chloride necessary for carrying out the reaction varies. Thus, according to one of the patents, the reaction was carried out in the presence of 3 wt. % of aluminium chloride[310].

The ease with which the radical replaces the hydrogen is determined by its affinity for the pair of electrons constituting its link with the benzene nucleus. The methyl group, therefore, is held more firmly than, for example, the butyl group[326]. Brown and coworkers[321], having investigated the question of orientation in the alkylation of the benzene nucleus in the presence of aluminium chloride, suggested that the place taken by the alkyl radical is determined not only by the distribution of electron density in the nucleus of the aromatic component, which depends on the substituents already present, but also by the nature of the attacking agent. The authors consider that the more reactive the carbonium ion formed (i.e. the less the relative ease of its formation), the less selectively it acts. If the carbonium ion is formed easily, its activity is more selective, and the *m*-isomer is obtained in insignificant quantity.

Apart from the catalysts mentioned above, the hydrogen halides themselves, and also boron fluoride, may be used in the synthesis of alkylphenols. The hydrogen halides have been used as catalysts only in the cases where the alkylating agent is a tertiary alkyl halide, taken as such, or arising by the action of the hydrogen halide on an unsaturated hydrocarbon. Thus, for example, there is a series of patents on the preparation of *o*- and *p*-(α-phenylalkyl)-phenols by the alkylation of phenol and catechol with 2-arylalk-1-enes in the presence of hydrogen chloride or bromide[327-329]. t-Butylphenol was obtained in a yield of 85% by the reaction of t-butyl chloride with phenol in the presence of hydrogen fluoride[330]; its yield in the presence of hydrogen chloride reached 90%[331]. But Simons[331] showed that the reaction of phenol and t-butyl chloride occurs on boiling the reactants even in the absence of a catalyst; the yield of *p*-t-butylphenol in this case amounted to 67%; t-pentylphenol was obtained in a similar way in a yield of 72%. Hart[332] considered that the alkylation of phenols by alkyl halides in the absence of a catalyst is, in fact, catalytic, the role of catalyst being played by the hydrogen halide evolved during the reaction. It was shown that in a dilute solution of *o*-dichlorobenzene at 60°, an autocatalytic alkylation of phenol and of *o*-cresol by triphenylchloromethane takes place[332]. The following reaction mechanism was suggested:

$$(C_6H_5)_3CCl \underset{\text{rapid}}{\rightleftharpoons} (C_6H_5)_3C^+ + Cl^-,$$

$$(C_6H_5)_3C^+ + \text{C}_6\text{H}_4(\text{OH})\text{H} \xrightarrow[\text{slow}]{} (C_6H_5)_3C\text{—C}_6\text{H}_4\text{—OH} + H^+.$$

The first reaction is made possible by the presence of an ionising medium (for example, phenol itself). The action of the hydrogen chloride formed is similar to that of the usual acid catalyst. The authors consider that, under their conditions, there occurs a direct alkylation of the nucleus, by-passing the ether stage, inasmuch as even under such mild conditions the ether decomposes. Therefore, although the alkylation on the oxygen goes more quickly, as a consequence of its reversibility, alkylphenols will accumulate in the products. Approximately the same yield of *p*-t-butylphenol (80%) is obtained in the reaction of t-butyl chloride with phenol in the presence of boron fluoride[333]. Hart[334] made the very interesting observation that the reaction of tertiary butyl chloride with phenol is prevented by the presence in the latter of dioxane as an impurity. The authors explain this fact by the removal of the phenol from the sphere of interaction with the alkyl halide on account of the formation of hydrogen bonds with the dioxane. Tertiary butyl chloride reacts with 3-t-butylphenol at 50°–60° in the absence of a catalyst, giving 2,5-di-t-butylphenol in quantitative yield. Spectroscopic investigations showed the complete absence of the *p*-isomer[335] in the reaction products.

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Published data on the alkylation of phenols by alkyl halides show that alkylation in the presence of aluminium chloride has been most thoroughly investigated. However, it must be borne in mind that isomerisation of the radical entering the phenol molecule does not always take place [isomerisation of *O*-alkyl- to *C*-alkyl-phenol? (Ed. of Translation)]. Alkylation by tertiary alkyl halides in the presence of hydrogen halides is very convenient, particularly in cases where the alkyl halide is formed during the synthesis, which makes it possible to use the more accessible alkenes as starting materials.

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SURFACE PHENOMENA IN THE DEFORMATION AND FRACTURE OF METALS

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1

In the deformation† and fracture of solid bodies an important part is played by small quantities of surface-active substances present in the surrounding medium or forming a component of the solid itself. The basis of this phenomenon, termed the Rebinder effect, is a decrease in the free energy of the new surfaces, formed and developed in the course of deformation and fracture of the solid, owing to reversible (physical) adsorption of surface-active molecules or atoms; this facilitates the development of such new surfaces and leads to a considerable reduction in the forces required to deform and fracture the body[1-17].

Adsorption may occur in various ways: adsorbed films may be formed on the external surfaces of the body by direct approach of surface-active material from the surrounding medium, or else such films may arise on internal micro-surfaces (on the walls of micro-cracks) as a result of rapid penetration of adsorption-active atoms inside the body by surface diffusion (migration) along defects in the crystal structure — the boundaries of blocks and grains, hollow dislocation centres, etc.[4,5,11,15,16,18]. Linear and two-dimensional structural defects, having an excess of free energy, serve as points for the selective adsorption of surface-active atoms arriving from the external surface or from the bulk of the material; in consequence, the behaviour of these defects during the course of deformation of the body is changed, e.g. their mobility is altered or their growth favoured, with the formation of a large free surface[15,19].

These changes in mechanical properties under the influence of adsorption have nothing to do with corrosion processes (including intercrystalline corrosion in polycrystalline solids), since they are produced by chemically inert media or by impurities present in extremely small amounts[5,11]; nor are these effects connected with dissolution, since the solids studied are either completely insoluble in the media or else (if a thin coating of molten metal acts as the medium) their solubility is low and, owing to the small mass of the coating, cannot lead to any substantial change in the specimen as a whole. Further, these effects relate to the surface of the metal itself, and are not due to the presence of oxide films, which can have only an incidental effect[5,20].

† In this review terms like deformation, strain, extension, etc. are often used synonymously (Ed. of Translation).

The development of a change in mechanical properties due to adsorption depends on several physicochemical factors, and primarily on the surface activity of the medium (or component) in relation to the given solid[6,11-14], i.e. on the absolute decrease in free surface energy resulting from adsorption. In addition, the experimental conditions — especially the temperature and the rate of deformation — profoundly influence the development on the effect[10,21-24]. Depending on these factors, the effect of surface-active substances on deformation and strength properties may take several quite different forms[13,14,24]. Thus an adsorption-active medium may soften the solid (metallic specimen); in such a case the yield point, and also the strain hardening in experiments with a constant rate of extension, is reduced or the rate of creep is increased in constant-load tests[5,23,24]. In other cases adsorption leads to the appearance of extreme brittleness in very plastic materials (single crystals of metals), accompanied by a sharp reduction in strength[11,12,22,25]. Under the influence of a strongly surface-active medium a solid may in certain circumstances show a tendency to disperse spontaneously into particles of colloidal dimensions[6,11-14].

Effects of the type under discussion find important practical application in the working of metals by pressure[26,27] and by cutting[28], in the find grinding of solids[7,8], etc. The study of these phenomena forms part of a new border-line science — the physicochemical mechanics of solids — developed by P. A. Rebinder and his collaborators, bordering on molecular physics, solid-state physics, physical chemistry, and the mechanics of continuous media. It has the aim of producing solids of specified structure and mechanical properties and of developing systematic methods for the mechanical working of solids by utilising physicochemical factors[6,29].

Single crystals of metals (including high-purity metals) provide the most interesting and also the simplest material for studying the effect of surface-active agents. In this case it proves possible to elucidate the most general and characteristic laws governing the observed phenomena, without complications due to grain boundaries, the presence of interfaces between different solid phases, and other subsidiary factors. At its present stage of development, the modern theory of the plastic deformation of crystalline solids — the theory of dislocations — which enables the mechanism of the action of the medium on the deformation and strength charaeteristics of a solid to be analysed[13-15,19,30], mainly in semi-quantitative terms, can be most usefully applied to materials of this kind. Such experiments will be examined in this survey.

2

The softening of metallic single crystals by organic adsorption-active media has been described in several papers[3-5,9]. Most authors have used dilute solutions of saturated and unsaturated aliphatic alcohols and acids and their substituted derivatives (i.e. substances whose molecules contain a polar group and a long hydrocarbon chain, such as oleic acid, palmitic acid, cetyl alcohol, etc.) in a non-polar hydrocarbon solvent (e.g. liquid paraffin). Experiments have been made on single crystals of tin, aluminium, and lead with extension both at a constant rate on a Polanyi type of apparatus and also under constant load. In the former case the effect of the medium is shown by a considerable decrease, almost to half, of the yield point (or crystal shearing stress) and of the strain-hardening (Fig. 1),