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ALKYLATION OF CYCLOALKANES, OXACYCLOALKANES, AND ARALKANES

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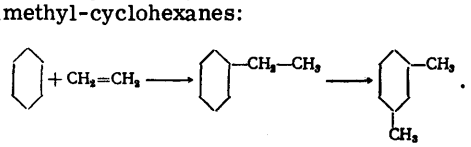
1. INTRODUCTION

Advances in the chemistry of fuel are closely connected with the development of studies in the field of alkylation. Beginning with the middle of the nineteenth century, work on the alkylation of aromatic hydrocarbons became widely known. The search for new methods of synthesis of high-octane components led to the discovery of alkane alkylation reactions. The extensive experimental data in this field have been described systematically in a number of reviews.

Comparatively recently new fields of application of the alkylation reaction have been discovered. This reaction has been extended to the alkylation of cycloalkanes, cyclic ethers (oxacycloalkanes), and the side-chain of aliphatic-aromatic hydrocarbons (aralkanes).

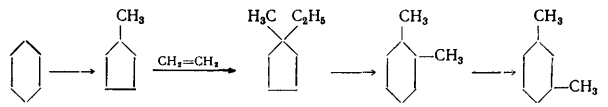
2. ALKYLATION OF CYCLOALKANES IN THE PRESENCE OF ACID CATALYSTS

In the presence of acid catalysts the composition of the alkylation products depends on the structure of the cycloalkane and the nature of the catalyst. When cyclohexane is alkylated with ethylene in the presence of aluminium chloride at 50–75°, a mixture containing 1,3-dimethylcyclohexane, tetramethylcyclohexane, and hexaethylbenzene was obtained[1] instead of the expected ethylcyclohexane. In Ipatieff's view, the absence of the direct alkylation products, ethylcyclohexane and diethylcyclohexane, can be explained by their isomerisation to dimethyl- and tetramethyl-cyclohexanes:



This hypothesis is consistent with the data of Grignard[2], who showed that in the presence of aluminium chloride, ethylcyclohexane indeed isomerises to dimethylcyclohexane. The presence of hexaethylbenzene in the catalytic reaction mixture proves the intermediate formation of hexaethylcyclohexane, which is then dehydrogenated under the reaction conditions[3].

Schmerling[4] holds a different view. He believes that the alkylation process is preceded by the isomerisation of cyclohexane to methylcyclopentane after which the alkene adds to the tertiary carbon atom:



This mechanism is supported by the fact that, in the presence of boron trifluoride, cyclohexane does not react with ethylene, since, unlike aluminium chloride, boron trifluoride does not cause the isomerisation of cyclohexane to methylcyclopentane under the alkylation conditions. The formation of hexaethylbenzene is explained by the dehydrogenation of cyclohexane and subsequent alkylation of benzene.

In the alkylation of cyclohexane with propene[5] in the presence of aluminium chloride at 10–45° polymethylated cyclohexane, dicyclohexyl, alkylated dicyclohexyl, and 2,6-dimethyldecalin are formed in the catalytic reaction mixture[6]. The propylcyclohexane formed in the alkylation of cyclohexane isomerises to polymethylated cyclohexane. The alkylation of cyclohexane with isobutene proceeds with more difficulty, since under the reaction conditions the latter tends to polymerise[5]. In the reaction between cyclohexane and di-isobutene in the presence of aluminium chloride, alkylated cyclohexanes boiling in the range 170–250° were obtained[7].

After passing a mixture of cyclohexane and ethylene over Ni/Al_2O_3 at 300°, 5% of toluene was isolated from the reaction mixture[8]. According to Komarewsky, cyclic hydrocarbons are not alkylated under the conditions described. The formation of toluene is explained by the dehydrogenation of cyclohexane to benzene[9], the alkylation of the latter with ethylene to ethylbenzene, and the decomposition of ethylbenzene with formation of toluene and methane[10].

When an equimolar mixture of cyclohexane and ethylene is passed over Cr_2O_3/Al_2O_3 at 475°, ethylbenzene is formed[11].

In the presence of sulphuric acid, neither cyclopentane nor cyclohexane react with alkenes[12,13].

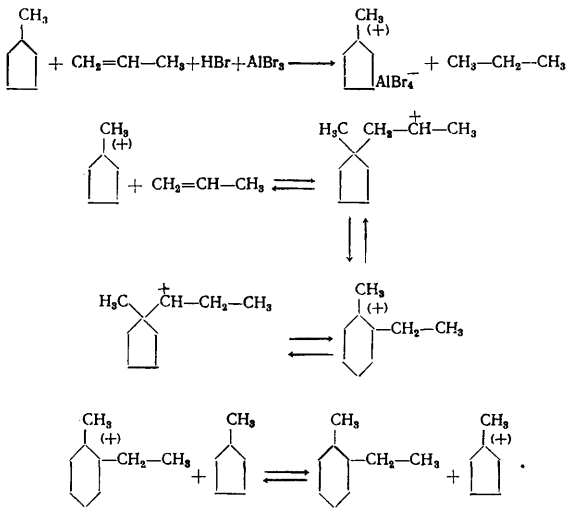
A number of patents[14-16] describe the alkylation of cycloalkanes with alkenes in the presence of mercaptans and a small amount of oxygen. The process is carried out at 300–450° and a pressure of 150–175 atm. The effects of pressure, component ratio, and various promoting agents have been investigated. Under optimum conditions the degree of reaction of the alkenes reaches 79%.

It is also recommended that cycloalkanes be alkylated in the presence of phosphoric acid on carriers[17] and catalysts based on hydrofluoric acid and alkali metal fluorides[18,19]. Ipatieff and Grosse[20] patented a method of alkylating three- and four-membered cycloalkanes with propene and butene in the presence of sulphuric and phosphoric acids, zirconium chloride, boron trifluoride, and activated clay. According to Levitt's data, the reaction of cyclopropane with t-butyl chloride in the presence of aluminium chloride results in the formation of a mixture of products having the composition $C_7H_{15}Cl$.[21,22]

In the presence of acid catalysts six-membered alkylcycloalkanes react with alkenes more readily than the unsubstituted compounds, forming the corresponding dialkylcycloalkanes. In the alkylation of alkylcyclopentanes the ring isomerises to a six-membered ring, and products of direct alkylation are not observed in the alkylation mixture.

According to the data of Ipatieff et al.[23], ethylene reacts with methylcyclohexane and methylisopropylcyclohexane in the presence of aluminium chloride (70°, 15 atm) and also with methylcyclohexane and methylcyclopentane in the presence of boron trifluoride (30°, 15 atm).

The alkylation of methylcyclopentane with propene in the presence of aluminium bromide at -42° was studied by Pines and Ipatieff[24]. Alkylated cyclohexane with the composition C_9H_{18} and other hydrocarbons with the composition $C_{12}H_{22}$ were isolated. The hydrocarbon C_9H_{18} proved to be 1-ethyl-2-methylcyclohexane, which is formed by the following mechanism:



The structures of 1-cyclohexyl-3-methylcyclopentane and 1-cyclohexyl-2-methylcyclopentane were attributed to the hydrocarbons with the composition $C_{12}H_{22}$. However, in later studies it was shown that these hydrocarbons consist of a mixture of 2,3- and 2,6-dimethyldecalins[25,26].

In 1944 Pines and Ipatieff patented a method of alkylating methylcyclopentane with propene in the presence of phosphoric acid at 100–400°[27] or boron trifluoride promoted by hydrofluoric acid at 30–50°.[28]

In the alkylation of methylcyclopentane with butenes, pentenes, and octenes in the presence of sulphuric and hydrofluoric acids, direct alkylation products could not be detected in the catalytic reaction mixture[29-31]. The authors of these studies explained their results by postulating that the main reaction is accompanied by a number of side-processes, such as the expansion of five-membered rings, dehydrogenation of cycloalkanes and hydrogenation of alkenes, isomerisation of alkenes with subsequent hydrogenation to isoalkanes, depolymerisation and dealkylation, and dehydrogenation of cycloalkanes with formation of polycyclic hydrocarbons.

The main product of the alkylation of methylcyclopentane with butene in the presence of sulphuric acid at 10–17° is a mixture of 1-ethyl-3,5-dimethyl- and 1-ethyl-3,4-dimethyl-cyclohexanes (83%). In the alkylation of methylcyclopentane with isobutene under the same conditions 10% of alkylated cyclohexane and 31% of polycyclic compounds were obtained. In the alkylation of methylcyclopentane with di-isobutene 4% of alkylcyclohexane and 60% of di- and poly-cyclic hydrocarbons were formed. Pent-2-ene enters into the reaction with greater difficulty than but-1-ene. Alkylated cycloalkanes, isopentane, decanes, and polycyclic hydrocarbons were obtained in the alkylation of methylcyclopentane with 3-methylbut-1-ene.

In the presence of hydrofluoric acid at 10° methylcyclopentane almost does not react with but-1-ene. When the reaction temperature was raised to 60°, alkanes, 1-ethyl-2,4-dimethylcyclohexane, and dicyclic hydrocarbons were isolated.

Schneider[32] alkylated methylcyclopentane, dissolved in isobutane or isopentane, with propene and isobutene in the presence of hydrofluoric acid. The main reaction product was tetramethylcyclohexane. Under similar conditions methylcyclohexane does not react either with isobutene or but-2-ene. The main product of the alkylation of methylcyclohexane with propene in the presence of aluminium chloride was a mixture of 1-methyl-3-propyl- and 1-methyl-4-propyl-cyclohexanes; polymethylated cyclohexanes were not detected.

Chernevskaya[33] showed that in the alkylation of methylcyclohexane with octyl chloride over a period of 6 h at 90° in the presence of aluminium chloride *gem*-methyloctylcyclohexane forms in 30% yield. Schmidl's patent[34] deals with the preparation of synthetic lubricating oils by the reaction of cycloalkanes with olefins in the presence of aluminium chloride.

Aluminium chloride has been suggested as the catalyst for the alkylation of methylcyclohexane with alkyl halides at 20–80°. A small amount of chlorocyclohexane forms together with alkylcyclohexanes[35]. Ethylmethylcyclohexane was obtained in the alkylation of methylcyclohexane with ethylene over a period of 6 h at 160–195° and a pressure of 65 atm. Mixtures of thorium oxide, aluminium chloride, and a metal (magnesium, sodium, or aluminium) have been recommended as catalysts for the process[36].

In the reaction between methylcyclohexane and ethylene in the presence of a mixture of stannous chloride and aluminium chloride a mixture of ethylmethylcyclohexane, trimethylcyclohexanes, and tetramethylcyclopentanes is formed. In the absence of aluminium, there is virtually no alkylation[37]. For the alkylation of methylcyclohexane with propene, Appell[38] proposed a mixed catalyst consisting of aluminium chloride and aluminium with added iron, cobalt, nickel, or tin. 1-t-Butyl-4-methylcyclohexane was obtained in the reaction between methylcyclohexane and isobutene at 0–25° in the presence of sulphuric acid[39]. McAllister and Bullard[40] alkylated alkylcycloalkanes with cyclopentene and cyclohexene in the presence of sulphuric acid promoted with benzenesulphonic acid or a mixture of sulphuric and phosphoric acids. In a study of the alkylation of methylcyclohexane with propene in the presence of sulphuric acid, Mamedaliev and Kuliev[41] showed that, in contrast to paraffinic hydrocarbons, the hydrogen of the tertiary carbon atom of methylcyclohexane is not substituted by an alkyl group: the catalytic reaction mixture does not contain *gem*-disubstituted cycloalkanes. In the alkylation of methylcyclohexane, ethylcyclohexane, and isopropylcyclohexane with propene and isobutene in the

presence of sulphuric acid at 0–60° up to 20–30% of dialkylcyclohexanes is formed, mainly 1,4-isomers, and 15% of polyalkylcyclohexanes[12,13]. Thus in the reaction between methylcyclohexane and propene 1-isopropyl-4--methylcyclohexane was obtained.

Unlike the other substituted cyclohexanes investigated, t-butylcyclohexane is not alkylated by alkenes in the presence of sulphuric acid, which may be due to steric hindrance caused by the t-butyl group.

In the alkylation of methyldecalin with propene in the presence of sulphuric acid[42,43], it was found that under the optimum conditions (30° and molar ratios sulphuric acid : methyldecalin : propene = 2 : 1 : 1) the alkylation mixture contains 20% of isopropylmethyldecalin. In the reaction between decalin and ethylene in the presence of aluminium chloride[44], a reaction mixture of complex composition was obtained from which it proved possible to isolate only a small amount of **2-ethyldecalin.**

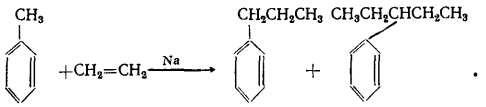
Chernevskaya[33] studied the alkylation of decalin with alkyl halides in the presence of aluminium chloride at 100°. A study was made of the effect of temperature, duration of the reaction, amount of catalyst, and the proportions of the reactants. As the amount of catalyst was increased, there was an increase in the yield of the reaction products but the content of the desired product fell. With the increase in the decalin : alkyl halide ratio from 1 : 1 to 10 : 1, the yield of alkyl derivatives increased to 30%. The maximum yield of the alkylation products was obtained in the presence of 2% of catalyst. The main products of the reaction are disubstituted derivatives.

The alkylation of aromatic compounds in the presence of acid catalysts is well known[45,46]. In the presence of acid catalysts, aralkanes are alkylated in the ring. A study has been made of the ethylation of toluene in the presence of mixed catalysts. Only traces of *p*-propylbenzene and 3-phenylpentane are formed at 300° on an aluminium–chromium catalyst. In the presence of an aluminium–molybdenum or an aluminium–cobalt–molybdenum catalyst the ring is alkylated. Both types of alkylation are observed to a small extent in the presence of an aluminium–platinum catalyst. In all cases the ethylene was also polymerised[47].

Much work has been done on the alkylation of tetralin, which, as regards its properties, can also be classified as an aralkane. The catalysts used in these reactions were phosphoric[48], hydrofluoric[49], and sulphuric[50] acids, aluminium[51], aluminosilicate[52], aluminium chloride[50], zinc chloride[52], etc. It has been established that in the presence of acid catalysts only the aromatic ring is alkylated.

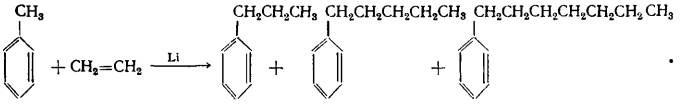
3. ALKYLATION OF ARALKANES IN THE PRESENCE OF BASIC CATALYSTS

In 1928 Hofmann and Michael[53] showed that aliphatic aromatic hydrocarbons can be alkylated by diolefins in the presence of alkali metals and their alloys. The alkylation of toluene and tetralin with butadiene in the presence of sodium was described as an example. Later Whitman[54] showed that aliphatic-aromatic hydrocarbons (toluene, cumene, tetralin) and unsaturated cyclic compounds (cyclohexene, cyclopentadiene) can be alkylated at 150–450° and a pressure of 50–3000 atm in the presence of 0.1–2% of an alkali metal. Thus in the alkylation of toluene with ethylene over a period of 17 h at 225° in the presence of sodium, n-propylbenzene and 3-phenylpentane were obtained:



The alkylation of ethylbenzene with styrene in the presence of sodium[57] gave 1,3-diphenylbutane as the main product. It has been established[55,56] that the yield of the monoalkylated derivative increases on addition of powdered iron. Pieper and Wegler[58,59] extended this reaction to nitrogen--containing heterocycles (picoline, quinaldine, 2-methylbenzothiazole). In the reaction of 370 g of picoline with 200 g of butadiene in the presence of 7 g of sodium over a period of 1 h at 100–120° 160 g of the monoalkenyl derivative and 100 g of the dialkenyl derivative was obtained.

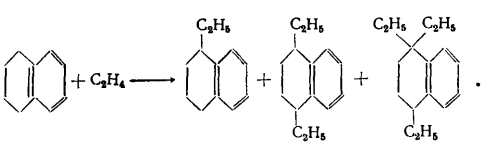
Fotis[60] showed that in the presence of lithium alkylation takes place at the terminal carbon atom of the side-chain of aliphatic-aromatic hydrocarbons. For example, in the alkylation of toluene (0.47 mole) with ethylene (68 atm) in the presence of lithium (0.075 mole) for 25 h at 250° 40% of **n-propylbenzene, 13.4% of 1-phenylpentane, 13.4%** of 1-phenylheptane, and 33.2% of a residue was obtained:



Later it was shown that the alkylation of the side chain of aliphatic-aromatic hydrocarbons can be carried out in the presence of organic alkali metal compounds. Little[61] alkylated toluene, tetralin, and cyclohexene in the presence of pentylsodium and phenylsodium.

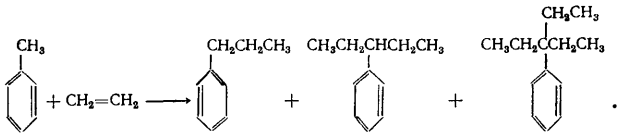
Pines and Ipatieff showed that the side chain of alkylbenzenes can be alkylated with alkenes in the presence of alkali metal acetylides[62], a mixture of an alkali metal and a nitrogen-containing compound[63], a mixture of alkali metals and an organic peroxide, and a mixture of an alkali metal and an organic compound of the general formula RX, where R = alkyl, alkenyl, cyclohexyl, and alkylphenyl, and X = OH, COOH, OR, NO_2, Cl, and CN[64–67]. Sodioanthracene proved to be the best catalyst.

Glosson et al.[68–72] alkylated cyclohexene, tetralin, toluene, and alkylheterocycles with alkenes in the presence of benzylsodium and sodiotetralin. Thus in the alkylation of cyclohexene with ethylene for 2.5 h at 125° in the presence of benzylsodium, 9.6% of 3-ethylcyclohexene was obtained. Under similar conditions isobutylbenzene was prepared from toluene and propene. The alkylation of tetralin was carried out in the presence of sodiotetralin at 140° and an ethylene pressure of 100 atm. The reaction yielded 21% of 1-ethyltetralin, 41% of **1,4-diethyltetralin,** and 8% of 1,1,4-triethyltetralin:



Pines et al.[73] alkylated toluene, ethylbenzene, propylbenzene, indane, and cyclohexylbenzene with ethylene in

the presence of sodioanthracene at 200–225° and a pressure of 30 atm. The alkylation of toluene gave *p*-propylbenzene, 3-phenylpentane, and 3-ethyl-3-phenylpentane:



Ethylbenzene reacts with ethylene to form s-butylbenzene (75%) and a small amount of 3-methyl-3-phenylpentane. The reaction of isopropylbenzene with ethylene gives t-pentylbenzene (78%). t-Butylbenzene does not react with ethylene. In the alkylation of cyclohexylbenzene, 1-ethylphenylcyclohexane was obtained (50%) while the alkylation of indane yielded 1-ethylindane (26%). It has been found that the reactivity of xylenes in the alkylation reaction decreases in the series *o*-xylene > *m*-xylene > *p*-xylene. The reaction with ethylene gives between 66 and 80% of the corresponding n-propyltoluenes. Cymene gives 62% of the monoalkylated derivatives which contain 72% of *p*-t-pentyltoluene. The alkylation of mesitylene gave 79% of 1,3-dimethyl-5-n-propylbenzene.

It has been shown, using the alkylation of toluene with ethylene as an example, that compounds which readily react with sodium, for example anthracene, fluorene, *o*-chlorotoluene, *o*-bromotoluene, and peroxides are satisfactory promoting agents.

According to a number of investigators, the mechanism of the alkylation of aliphatic-aromatic hydrocarbons, for example toluene, can be represented as follows (RX = molecule of promoting agent, X = halogen):

$$RX + 2Na \rightarrow RNa + NaX, \quad (1)$$

$$C_6H_5CH_3 + RNa \rightarrow C_6H_5CH_2Na + RH, \quad (2)$$

$$C_6H_5CH_2Na + CH_2{=}CH_2 \rightarrow C_6H_5CH_2CH_2CH_2Na, \quad (3)$$

$$C_6H_5CH_2CH_2CH_2Na + C_6H_5CH_3 \rightarrow C_6H_5CH_2CH_2CH_3 + C_6H_5CH_2Na, \quad (4)$$

$$C_6H_5CH_2Na + C_6H_5CH_2CH_2CH_3 \rightarrow C_6H_5CH_3 + C_6H_5CH(Na)CH_2CH_3, \quad (5)$$

$$C_6H_5CH(Na)CH_2CH_3 + CH_2{=}CH_2 \rightarrow C_6H_5CH\langle{}^{CH_2CH_3}_{CH_2CH_2Na}, \quad (6)$$

$$C_6H_5CH\langle{}^{CH_2CH_3}_{CH_2CH_2Na} + C_6H_5CH_3 \rightarrow C_6H_5CH(C_2H_5)_2 + C_6H_5CH_2Na. \quad (7)$$

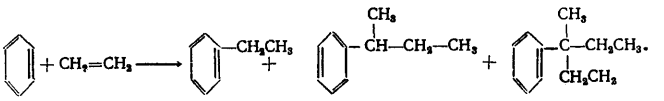
The reaction of promoting agents with sodium gives organosodium compounds which metallate the side-chain of the aliphatic-aromatic hydrocarbon. The resulting organosodium compound adds to ethylene with formation of a new organosodium compound which then metallates the initial hydrocarbon or the ethylated alkylbenzene, forming the monoalkylation product.

Later Pines and Mark[74] studied the reaction of aliphatic-aromatic hydrocarbons with various olefins in the presence of organosodium compounds at 300°. They showed that the reaction of but-1-ene and oct-1-ene gives 2-benzylbutane and 2-benzyloctane in up to 10% yields. Similarly the reaction of propene with toluene, ethylbenzene, isopropylbenzene, and diphenylmethane results in the formation of isobutylbenzene (10%), 3-methyl-2-phenylbutane (16.7%), 2,3-dimethyl-2-phenylbutane (7.8%), and 2-methyl-1,1-diphenylpropane (51%) respectively. 1,3-Diphenylpropane (21%), 1,3-diphenylbutane (12%), 1,3,5-triphenylpentane (29%), and 1,3,5-triphenylhexane (16%) are formed in the alkylation of toluene and ethylbenzene with styrene[75] in the presence of sodium at 110–125°. The yield of monosubstituted derivatives increases in the presence of promoting agents: benzylsodium, sodioanthracene, and sodium isopropoxide. For example, in the case of benzene the yield of monoalkyl derivatives increases from 21 to 40%. In the presence of promoting agents isopropylbenzene reacts with styrene, forming 9% of monoalkylated and 29% of dialkylated derivatives; in the absence of promoting agents polymers are formed.

Schaap and Pines[76] studied the alkylation of toluene, ethylbenzene, cumene, and cyclohexylbenzene with ethylene in the presence of the potassioanthracene catalyst. Cyclisation products were found in the catalytic reaction mixture together with monoalkyl derivatives. The yield of cyclisation products ranges from 2% for toluene to 43% for cumene. Addition of sodium to potassioanthracene increases the yield of alkylation products.

The reaction of isopropylbenzene with ethylene in the presence of metallic potassium gives only the alkylation product[77]. It is interesting that a mixture of potassium hydride and butyl-lithium is an active catalyst for both alkylation and cyclisation of the side-chain of aliphatic-aromatic compounds[78].

Podall and Foster[79] state that the toluene side-chain may be alkylated in the presence of graphite-potassium alloy. According to the data of Esmay et al.[80], in the presence of alkali metals on carriers benzene is alkylated with subsequent further alkylation of the side chains. Thus in the reaction of benzene with ethylene in the presence of Na/Al_2O_3 the products obtained were 10% of ethylbenzene, 40% of s-butylbenzene, and 30% of 3-methyl-3-phenylpentane:



Other catalysts which may be used are Na/C and Li/C and also potassium, sodium, lead, and caesium on MgO, ZnO, BaO, and CdO.[81] The alkylation does not take place in the presence of Na/NaCl and Na/TiO_2.

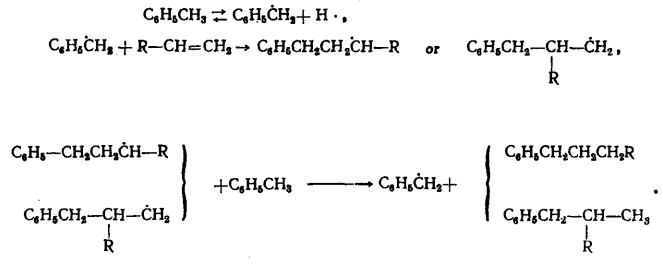
In many cases the alkylation of aliphatic-aromatic and unsaturated cyclic hydrocarbons can be achieved in the presence of alkali metal hydrides[82,83]. Thus Voltz[47] showed that the reaction of toluene with ethylene in the presence of sodium and lithium hydrides at 300° gives alkylation and polymerisation products. In the presence of calcium, strontium, and barium hydrides there is no alkylation. The hydrides of titanium and tantalum are ineffective in the alkylation of toluene at 300°. In the presence of zirconium hydride there is both alkylation of toluene and polymerisation of the alkene.

4. THERMAL AND INITIATED ALKYLATION OF CYCLOALKANES, OXACYCLOALKANES, AND ARALKANES

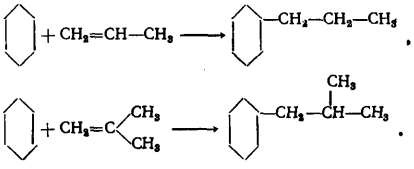
The side-chains of aliphatic-aromatic compounds are known to resemble in their chemical properties alkanes and therefore it might have been expected that it would prove possible to alkylate the side-chains of such hydrocarbons without involving their aromatic rings. Acid catalysts are unsuitable for this purpose, since in their presence the aromatic ring is in fact alkylated. By analogy with the behaviour of alkanes, Ipatieff et al.[84] attempted to

alkylate the side-chain of alkylbenzenes at a high temperature and pressure. It was shown that the alkylation of toluene with ethylene gives n-propylbenzene.

Subsequently this reaction was studied by Pines and coworkers[85-87]. The thermal alkylation of toluene (I), ethylbenzene (II), and cumene (III) was studied in a flow system at a pressure of 420 atm and 400–500° using a brief contact time and a molar ratio alkylbenzene : alkene of 5 : 1. As was expected, an asymmetric alkene gives two products, corresponding to addition to two different carbon atoms of the double bond. One of the products is formed in a greater amount, as happens in the alkylation of alkanes. The authors introduced the concept of "selectivity", i.e. the ratio of the yield of the product of addition to the more stable radical and the yield of the product of addition to the less stable radical. It was shown that the selectivity of addition of alkylphenyl groups to asymmetric alkenes decreases with decrease in the stability of the corresponding free radical. As in the thermal alkylation of alkanes, the reactivity of alkenes decreases in the series propene > > isobutene > 2-methylbut-2-ene, but-1-ene > but-2-ene. A free-radical mechanism, similar to that for the thermal alkylation of alkanes, was proposed for the formation of the monoalkylation products:



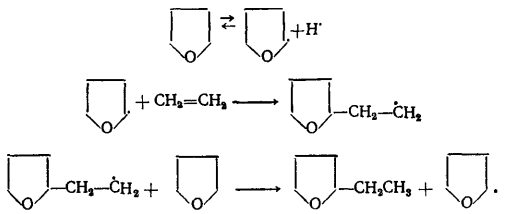
Recently the alkylation of cyclohexane[88] and cyclopentane[89] with alkenes was achieved at 450° at a pressure of 200 atm. Ethylcyclohexane, propylcyclohexane, and isobutylcyclohexane were isolated in the alkylation of cyclohexane with ethylene, propene, and isobutene respectively. It was found that at an elevated temperature cyclohexane adds to the most unsaturated carbon atom of the alkene:



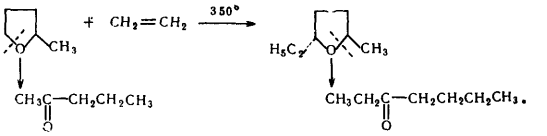
Study of the alkylation of methylcyclohexane with alkenes[90] at 350° and 50 atm showed that the main product of the reaction of methylcyclohexane with ethylene is a mixture of ethylmethylcyclohexanes. The reaction with propene proceeds with greater difficulty. Since it is known that a tertiary radical forms more readily than a secondary radical, it might have been expected that the alkylation of methylcyclohexane with ethylene would give 1-ethyl-1-methylcyclohexane. However, a mixture of 1-ethyl-3-methyl- and 1-ethyl-4-methyl-cyclohexanes was obtained instead.

In contrast to benzene, cyclohexane reacts with alkenes albeit at an elevated temperature and pressure. The different behaviour of cyclohexane and benzene in the alkylation process is shown clearly in the alkylation of tetralin. It might have been supposed[91] that under similar conditions tetralin should be selectively alkylated by olefins in the cycloparaffin ring, and this was confirmed experimentally. 1-Ethyltetralin and 1,4-diethyltetralin were isolated after alkylation of tetralin with ethylene at 450° and 200 atm; the alkylation with propene proceeds with greater difficulty.

In their study of the reaction of oxacycloalkanes (tetrahydrofuran, tetrahydrosilvan, tetrahydropyran) with various olefins at an elevated temperature, Shuikin and Lebedev[92] found that alkylation occurs in the temperature range 300–400°; below 300° there is virtually no reaction and above 400° decomposition processes predominate. A study was made of the effect of temperature, the duration of the reaction, and ethylene pressure on the degree of conversion of the oxacycloalkanes and the yield of monoalkyl derivatives. It is interesting that introduction of a methyl group into the tetrahydrofuran ring lowers the yield of the monoalkyl derivative. Apparently thermal alkylation of oxacycloalkanes, for example tetrahydrofuran, takes place by a free-radical mechanism, like the thermal alkylation of alkanes:



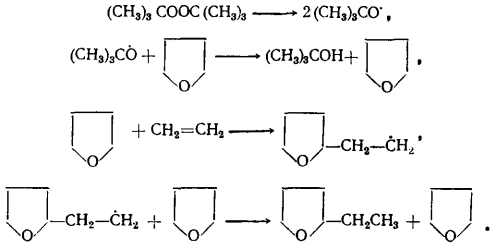
In their oxacycloalkane alkylation experiments, Shuikin and Lebedev[93] were the first to observe the thermal isomerisation of alkyl tetrahydrofurans. 2-Pentanone (the product of the isomerisation of the initial tetrahydrosilvan) and 3-heptanone (the product of the isomerisation of the 2-ethyl-5-methyltetrahydrofuran formed) were detected in the products of the alkylation of tetrahydrosilvan with ethylene at an elevated temperature:



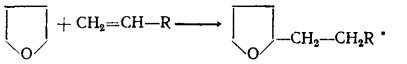
Ethylene is known to undergo polymerisation in the presence of peroxides[94], the rate of polymerisation increasing appreciably in the presence of ethers[95]. A number of patents describe the formation of polymerisation products in the reaction of cyclic ethers with unsaturated compounds. For example, the formation of heavy waxes in the telomerisation of ethylene with dioxan, tetrahydrofuran, dioxolane, and ethyl ether at 50–300° and a pressure of 400–1000 atm has been described[96].

According to the data of Hanford and Roland[97], the reaction of oxygen-containing compounds with ethylene in the presence of radical-forming initiators gave polymerisation products with the formula $R(CH_2CH_2)_nH$, where n is between 22 and 54. In particular, the reaction of dioxan with ethylene resulted in the formation of a product having the formula $C_4H_8O_2(CH_2CH_2)_{54}H$. The telomerisation of dioxolane with ethylene (600–900 atm) for 18 h at 100° in the presence of benzoyl peroxide yielded a wax having the composition $C_3H_6O_2(CH_2CH_2)_{44.5}H$.[98] The products of the reaction of dioxan with decene in the presence of benzoyl peroxide are used as lubricating oils[99].

Shuikin and Lebedev[100] showed that in the presence of di-t-butyl peroxide the reaction of oxacycloalkanes with unsaturated compounds occurs at a much lower temperature (150°). The radical mechanism of the alkylation and the initiating activity of peroxides is confirmed by the presence in the reaction products of t-butanol, which is formed as follows:



Using the alkylation of tetrahydrofuran and tetrahydropyran with hex-1-ene as an example, it was shown that a decrease of the concentration of the alkene results in an increase of the yield of the monoalkyloxacycloalkane. Thus when the tetrahydrofuran : hex-1-ene ratio is increased from 10 : 5 to 10 : 0.5, the yield of 2-hexylhydrofuran increases from 13.2 to 79.2%.[101,102] An increase of the length of the hydrocarbon chain of the alkene lowers somewhat the yield of the 2-alkyloxacycloalkane. The corresponding 2-ethyloxacycloalkanes were obtained in the alkylation of tetrahydrofuran, tetrahydropyran, and dioxan with ethylene in the presence of peroxide at 150°. In the presence of peroxide the alkene adds to oxacycloalkanes via its most unsaturated carbon atom. Thus in the alkylation of tetrahydrofuran with propene, hex-1-ene, hept-1-ene, and oct-1-ene in the presence of peroxide the corresponding 2-alkyltetrahydrofurans with a straight side-chain were obtained:



A similar situation is observed in the alkylation of tetrahydropyran with hex-1-ene and hept-1-ene.

According to Schmerling's data[103], in the presence of organic peroxides cycloalkanes interact with ethylene and form polymers. For example a polymer having the composition $C_6H_{11}(CH_2-CH_2)_nH$ was obtained in the reaction between cyclohexane and ethylene. It has been stated[104] that ethylene enters into a telomerisation reaction with toluene at 200° and a pressure of 140 atm when the process is initiated with cumenyl hydroperoxide.

Nikishin et al.[105] established that toluene, ethylbenzene, cumene, *p*-xylene, and α-methylnaphthalene are capable of adding to alkenes at 150–160° in the presence of t-butyl peroxide. The yield of the monoalkylation products is 10–15%. In the presence of tetraethyl-lead alkylbenzenes are alkylated by ethylene at the α-carbon atom of the side-chain[106].

Eidus and Ershov[107,108] showed that when mixed with carbon monoxide and hydrogen cyclohexene is methylated to the extent of 7–10% by CH_2 radicals formed on reduction of the carbon monoxide with hydrogen, and is converted into mono- and 1,2-di-methyl derivatives. Methylcyclohexene was also obtained in the alkylation of cyclohexene by methylene radicals formed by the hydrocracking of isobutene at 190° on a cobalt–clay catalyst[109].

The review of the literature dealing with the alkylation of saturated cycloalkanes shows that, in the presence of acid catalysts, the composition of the alkylation products depends on the structure of the cycloalkane and the nature of the catalyst. Thus in the presence of aluminium chloride, unsubstituted cyclohexane forms a mixture of polymethylated cyclohexanes. In the presence of sulphuric acid neither cyclopentane nor cyclohexane reacts with alkanes.

In the alkylation of alkylcyclopentanes in the presence of aluminium chloride or boron trifluoride expansion to a six-membered ring takes place; direct alkylation products have not been detected in the alkylation mixture. In the presence of sulphuric acid six-membered alkylcycloalkanes form the corresponding 1,4-dialkylcyclohexanes. In the alkylation of tetralin in the presence of acid catalysts the alkylating agent adds to the aromatic ring; under these conditions the cycloparaffin ring is not alkylated.

The study of the alkylation of saturated systems entered a new phase when it was found that the alkylation of cycloalkanes and the side-chain of aliphatic-aromatic compounds can be carried out in the presence of basic catalysts: sodium, sodioanthracene, benzylsodium, potassium, lithium, etc. Thus in the alkylation of toluene with ethylene in the presence of sodium propylbenzene is obtained and in the alkylation of tetralin in the presence of sodiotetralin ethylene adds to the cycloparaffin ring.

The need to obtain motor fuels with a higher octane number led investigators to attempt the thermal alkylation of alkanes. An industrial method has been developed for the preparation of neohexane by the thermal alkylation of isobutene with ethylene. Subsequently, assuming an analogy with the behaviour of alkanes, a study was made of the thermal alkylation of the side-chains of aliphatic-aromatic hydrocarbons, cycloalkanes, and oxacycloalkanes. The alkylation of the side-chains of aliphatic-aromatic hydrocarbons and oxacycloalkanes occurs under milder conditions in the presence of initiating substances. Chloroform, benzyl chloride, dichloropropane, and organic peroxides have been suggested as initiators.

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OUTER-SPHERE INTERACTION IN AQUEOUS SOLUTIONS OF COMPLEX COMPOUNDS

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1. INTRODUCTION

The majority of chemical processes in nature and technology take place in aqueous solutions. These processes are closely linked with complex formation.

Ions in water are present as simple aquo-ions or mixed complexes: hydroxoaquo-, oxoaquo-, halogenoaquo-, and similar compounds. Complex formation in solutions involves the replacement of ligands in the inner sphere of the so called "free" central ion. This replacement may take place with or without change in the geometric configuration of the inner sphere[1,2].

Complex compounds in solution are defined as any associated species whose components are joined by a direct bond[3], whose energy of formation is greater than, or at least only slightly less than, the kinetic energy of the solvent molecules[4]. Associated species in which there is no direct bond between the ions are called outer-sphere complexes or associated species of the ion-pair type[5].

The results of many studies[3] show that complex formation in solutions is not restricted to the Werner[6] coordination sphere. Complex ions which according to Werner's theory are coordinatively saturated may still combine with ions with opposite sign[3] and polar molecules[7].

In a number of complexes the stability of the inner-sphere bonds is comparable to and even slightly less than the stability of the outer-sphere bonds[3,8,9]. This situation is often encountered in complex formation in concentrated ($> 1\ N$) aqueous solutions of inert salts, but is sometimes also found in dilute aqueous solutions of complex compounds[10,11].

Data have been published on outer-sphere interaction in aqueous solutions of complex compounds in the presence and absence of inert salts, but there are no reviews or monographs on this subject. Moreover, technologists and many research workers, following Bjerrum[12], consider that the influence of outer-sphere ions on complex formation in aqueous solutions is non-existent or negligibly small relative to the effect of inner-sphere interaction, although there are not always sufficient grounds for this.

The present paper is an attempt to examine critically published data on outer-sphere interaction in aqueous solutions of complex compounds. The problem of standardising conditions for the study of outer-sphere association is discussed, a procedure for calculating outer-sphere association constants for labile[13] and relatively unstable ionic