U.D.C. 547.133:547.301

Effects of Steric Hindrance in Molecules on the Properties and Synthesis of Hydrocarbons

V.V.Voronenkov and Yu.G.Osokin

Data on the steric hindrance in hydrocarbon molecules have been reviewed. The effect of steric hindrance on the physical properties of hydrocarbons (specific gravity, refractive index, and refraction) and on their ultraviolet and ^{1}H NMR spectra has been demonstrated. The influence of steric hindrance on the synthesis of hydrocarbons in alkylation, oligomerisation, and polymerisation reactions has been examined. A theoretical explanation has been given for a number of reactions occurring anomalously under the influence of steric hindrance.
The bibliography includes 160 references.

CONTENTS

I. Introduction 616
II. The nature of steric hindrance 616
III. Steric hindrance in the synthesis of hydrocarbons 621

I. INTRODUCTION

Hydrocarbons are a valuable starting material for the main products of large-scale organic synthesis[1]. At the same time they are convenient for the investigation of steric hindrance in molecules. This is because in hydrocarbons interactions of other types are reduced to a minimum. Therefore, when steric hindrance arises in molecules, its effect is shown most clearly in hydrocarbons. In the literature[2-10] dealing with the study of compounds of this class, the important role of steric hindrance in chemical reactions of hydrocarbons has been frequently pointed out. However, so far there have been almost no systematic descriptions of data on this problem. This review deals with the effect of steric hindrance on the physicochemical properties and synthesis of hydrocarbons.

II. THE NATURE OF STERIC HINDRANCE

Examination of numerous literature data for hydrocarbons leads to the conclusion that steric hindrance alters their molecular geometry, which entails an increase of the internal energy of such molecules, so that among the isomers of hydrocarbons, sterically hindered structures become thermodynamically less stable.

The change in molecular geometry takes place in the following three ways: rotation about the bonds with the displacement of one part of the molecule from the plane of the other, deformation of valence angles in the plane, and extension of the bonds between atoms.

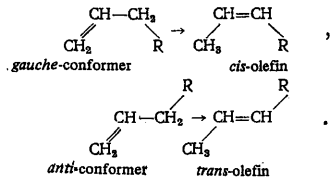
The changes undergone by the molecule under the influence of steric hindrance occur simultaneously. However, since the extension of bonds requires a much larger energy than does rotation about a single bond and the deformation of the valence angle of such a bond, it evidently follows that the first two types of geometrical changes will be mainly observed.

1. Rotational Isomerism in Hydrocarbons

When the distribution of atoms in space was considered in terms of classical stereochemistry, account was taken only of the interatomic distances and valence angles. Although this made it possible to understand many features of the structure and chemical behaviour of hydrocarbons, no less significant results in this field were achieved after the appearance of conformational concepts[9-13].

Interesting electron diffraction studies on the conformations of hydrocarbon molecules in the gas phase were carried out by Vilkov and coworkers[14]. In the determination of the energetically favourable molecular conformation, they took into account not only the repulsion between atoms not linked by valence bonds but also the interaction between the bonds in the molecule. Table 1 presents the preferred conformations of the rotational isomers of a number of hydrocarbons, taking into account the above factors.

For propene, but-1-ene, and other α-olefins, the eclipsed and *gauche*-conformations predominate. This has been demonstrated in a study of the ^{1}H NMR spectra[15] of but-1-ene, pent-1-ene, and hex-1-ene and has been confirmed by calculation[16]. In the ground state of liquid alk-1-enes the *gauche*-conformations predominate, but, on passing to olefins with a more bulky group R, the *anti*-conformations become more stable owing to a reduced steric hindrance. Such distribution of conformations accounts satisfactorily for the experimentally observed[17,18] *cis*-stereospecificity of the positional isomerism of various olefins.



Studies on a number of conjugated dienes by ultraviolet spectroscopy[19] revealed a transoid conformation of the sterically unhindered alkyl-substituted diene hydrocarbon. The *trans*-configuration of such hydrocarbons is additionally stabilised by the maximum degree of π,π conjugation.

Evidently the conjugation effect is responsible for the stable configurations of phenylcyclobutane and phenylcyclopropane, since the "banana bonds" of the latter are capable of conjugation with the aromatic ring. The rotational isomerism of alkyl derivatives of cyclic hydrocarbons is important[20-23]. Its effect on the reactions of

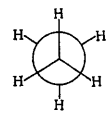
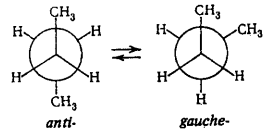
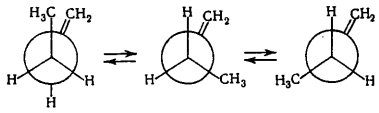
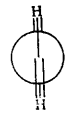
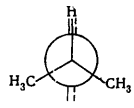
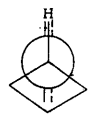
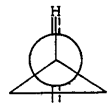
cyclic hydrocarbons has been examined in a review by Bragin and Liberman [10].

At the present time conformational analysis of hydrocarbons has developed so much that it has now become possible to make satisfactory predictive calculations of the energetically favourable conformations [16,28,29]. Thus, according to Kitaigorodskii [28], the potential energy which determines the conformational properties of molecules consists of the energy of interaction (repulsion) between atoms not linked by valence bonds and the elastic energy of the valence angles. The optimum conformation should correspond to an energy minimum and should arise from a compromise between the tendency of the non-bonded atoms to move apart to equilibrium distances and the tendency of the valence angles to retain the ideal values. In this connection it is of interest to quote a statement by A.A. Chugaev who wrote as early as 1904 "Chemical molecules represent [are a result of] a mechanism involving a certain energy store. In order to understand the operation of such mechanisms, it is necessary to know to an equal extent their internal structure and the distribution of energy in them" [30].

Kitaigorodskii calculated the most favourable conformations of certain hydrocarbons (bicyclic terpenes). Kitaigorodskii's method makes it possible to predict accurately the deviations of the C–C–C angles in alkanes from the tetrahedral value to 112.5°.

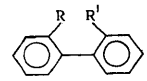
Using Kitaigorodskii's concepts, Dashevskii [29] developed a method for the calculation of the energies of formation of hydrocarbon molecules from atoms. He calculated the geometries and atomisation energies of straight-chain alkanes and their isomers.

Table 1. Stable conformations of the rotational isomers of various hydrocarbons.

Hydrocarbon	Conformation of isomer	References
Ethane		24
Butane	 *anti-* *gauche-*	12,13
Propene		14,25
α-Butene		14
Butadiene		14
Cumene		26
Phenylcyclobutane		26
Phenylcyclopropane		27

2. Atropisomerism of *oo'*-Dialkyl-substituted Biphenyls

A special case of conformational isomerism is the atropisomerism of *oo'*-disubstituted biphenyls:



As a result of the interaction of the groups R and R' in the *oo'*-positions of biphenyl, rotation of the benzene rings about the common axis becomes impossible; therefore the molecule becomes asymmetric and optical isomerism appears. Thus Meisenheimer [31] and Mills [32,33] showed by calculation that the presence of methyl groups in the *oo'*-positions is sufficient to hinder rotation. According to the Adams empirical rule, the resolution of biphenyls into optical isomers is possible when the sum of the C–R and C–R' bond lengths is greater than 2.90 Å. The steric hindrance in *oo'*-dialkylbiphenyls and their steric strain increase fairly rapidly with increasing branching of the alkyl group. Therefore the synthesis of *oo'*-di-t-butylbiphenyl is extremely difficult [34].

3. Effect of Steric Hindrance on the Physical and Chemical Properties of Hydrocarbons. The Auwers–Skita rule

The first constant widely used in organic chemistry to assess the molecular structure of hydrocarbons was molecular refraction. It was noted that the refraction of *o*-dialkylbenzenes is lower than the refractions of the corresponding *m*- and particularly *p*-isomers [35,36]. Since molecular refraction is proportional to atomic volume [37], its lower value for *o*-dialkylbenzenes is evidence of a denser packing of the atoms of the alkyl groups in their molecules compared with the *m*- and *p*-isomers. This conclusion is confirmed by the finding that *o*-dialkylbenzenes have higher densities, refractive indices, and boiling points than the *p*-substituted derivatives where there is no steric hindrance (Table 2).

Thus a kind of steric "contraction" (condensation) is observed in *o*-dialkylbenzenes, due to the interaction of adjacent alkyl groups not linked by valence bonds (the "ortho-effect"). Such "contraction" results in the appearance of repulsion forces which hinder the rotation of the alkyl groups about the single $C_{ar}-C_{alk}$ bond, leading to the deformation of the angles between these bonds and an increase of the internal energy of the molecule [38-39].

o-Dialkylbenzenes are geometrically similar to *cis*-olefins and the *p*-isomers are similar to *trans*-olefins (the Werner rule [40]). This analogy is reflected also in the

physical properties. The densities, refractive indices, and boiling points of *cis*-olefins, like those of *o*-dialkylbenzenes, are higher than for the *trans*-isomers; at the same time the molecular refractions of *cis*-olefins are lower than those of *trans*-olefins (Table 3).

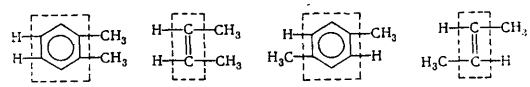


Table 2. Physical constants of *o*- and *p*-dialkylbenzenes.

Hydrocarbon	MR_D, cm^3	B.p., °C	ρ_4^{20}, g cm^{-3}	n_D^{20}
p-Xylene	36.02	138.35	0.8610	1.4958
o-Xylene	35.77	144.41	0.8802	1.5054
p-Cymene	45.34	177.25	0.8573	1.4909
o-Cymene	45.04	178.35	0.8766	1.5000
p-Diethylbenzene	48.82	183.75	0.8619	1.4948
o-Diethylbenzene	48.53	183.42	0.8799	1.5026

Thus a steric "contraction" of alkyl groups analogous to that in *o*-dialkylbenzenes is observed in *cis*-olefins. It has been shown by ^{1}H NMR [42] that in *cis*-but-2-ene there is indeed an appreciable overlapping of the van der Waals spheres of the methyl groups, which does not happen in the *trans*-isomer.

Table 3. Physical constants of *cis*- and *trans*-olefins [41].

Hydrocarbon	MR_D, cm^3	B.p., °C	ρ_4^{20}, g cm^{-3}	n_D^{20}
trans-Pent-2-ene	25.61	36.35	0.6432	1.3793
cis-Pent-2-ene	25.38	36.94	0.6555	1.3898
trans-Hex-2-ene	29.59	67.88	0.6779	1.3936
cis-Hex-2-ene	29.34	68.84	0.6872	1.3976
trans-Hex-3-ene	29.61	67.08	0.6770	1.3943
cis-Hex-3-ene	29.40	66.45	0.6799	1.3950

The overlapping of the van der Waals spheres leads to the mutual repulsion of the *cis*-alkyl groups, which in turn leads to an increase of the valence angles and of the strain in the double bond ("cisoid repulsive strain") [43]. The strain in the double bond can be estimated experimentally from thermochemical data by comparing the negative heats of hydrogenation of olefins (Table 4).

It follows from Table 4 that, with increase of the bulk of the alkyl groups in the *cis*-position of the olefin, the negative heat of hydrogenation also increases, which corresponds to a greater strain in the C=C bond and hence to a greater deviation of the C=C–C valence angle [from the ideal value], which amounts to 136° in *cis*-di-t-butylethylene. The main consequence of such strain in the double bond is an enhanced reactivity in reactions characteristic of the usual olefins. This interesting question has been discussed in detail in a review by Zefirov and Sokolov [43]. Steric hindrance is observed also in the series of monoalkylnaphthalenes [44]. α- and β-Substituted isomers are typical for these compounds, the relation between their physical properties being similar to that in *cis*- and *trans*-olefins or *o*- and *p*-dialkylbenzenes respectively. This can be inferred from the specific gravities, refractive indices, boiling points, and molecular refractions of alkylnaphthalenes (Table 5). However, one should note that, whereas the steric hindrance in *o*-dialkylbenzenes and *cis*-olefins is due to adjacent alkyl groups, in α-monoalkylnaphthalenes it arises due to "peri-hydrogen".

Table 4. Negative heats of hydrogenation of *cis*- and *trans*-olefin isomers.

Compound	ΔH_{hydr}, kcal mole^{-1}
cis-But-2-ene	28.5
trans-But-2-ene	27.5
cis-t-Butylmethylethylene	30.8
trans-t-Butylmethylethylene	26.5
cis-Di-t-butylethylene	36.2
trans-Di-t-butylethylene	26.87

In 1,2-*cis*-isomers of cyclic compounds [45], steric "contraction" is observed as in the *cis*-derivatives of ethylene. According to the Auwers–Skita rule [46], in the series of isomeric hydroaromatic compounds the *cis*-isomer has a higher density, refractive index, and boiling point and a lower molecular refraction and hence a lower molecular volume than the *trans*-isomer. However, the studies of Kazanskii and Liberman and coworkers [47–52] showed that this rule must be used with caution. They demonstrated for a large number of examples that the *cis*-isomers of dialkylcycloalkanes can also have boiling points lower than those of the *trans*-isomers.

Table 5. Physical constants of α- and β-alkylnaphthalenes.

Hydrocarbon	MR_D, cm^3	B.p., °C	ρ_4^{20}, g cm^{-3}	n_D^{20}
β-Methylnaphthalene	49.24	241	0.9904	1.6026
α-Methylnaphthalene	48.82	244.7	1.0203	1.6180
β-Ethylnaphthalene	53.88	252	0.9922	1.6028
α-Ethylnaphthalene	53.46	258.7	1.0081	1.6089
β-Isopropylnaphthalene	58.89	268	0.9780	1.5861
α-Isopropylnaphthalene	58.48	272	0.9762	1.5877
β-Butylnaphthalene	63.31	275	0.9750	1.5818
α-Butylnaphthalene	62.88	280	0.9768	1.5820

The steric hindrance in hydrocarbons has a significant influence on exaltation (EM_D). Bruhl [53,54], who introduced this concept, showed that exaltation occurs on bond conjugation, i.e. in the presence of an enhanced electron mobility in the molecule. The exaltation of *p*-dialkyl-substituted benzenes, *trans*-olefins [55], and β-monoalkyl-substituted naphthalenes [56] is much higher than the corresponding values for the *o*-, *cis*-, and α-substituted isomeric hydrocarbons—compounds with steric hindrance. Thus steric hindrance in the hydrocarbon molecule leads to a decrease of exaltation, i.e. to a decrease of the mobility of its electron system.

Another example of steric hindrance in the molecule affecting exaltation and hence also conjugation in hydrocarbons is provided by the phenomenon of "central depression" [57], the essential feature of which is that substitution of the hydrogen atom by alkyl groups in the centre

of a diene molecule leads to a decrease of exaltation compared with that of the diene hydrocarbon in which the alkyl groups are present at the edges (Table 6).

Table 6. Refractions and exaltations of certain diene hydrocarbons.

Compound	MR_D, cm^3		EM_D
	expt.	calc.	
trans-CH_3—CH=CH—CH=CH_2	25.97	24.35	1.62
cis-CH_2—CH=CH—CH=CH_2	25.40	24.35	1.10
CH_2=C(CH$_3$)—CH=CH_2	25.40	24.35	1.05
CH_3—CH=CH—CH=CH—CH_3	30.73	28.97	1.76
CH_2=CH—CH=C(CH$_3$)—CH_3	30.39	28.97	1.42
CH_3—CH=CH—C(CH$_3$)=CH—CH_3	34.59	33.59	1.00

The greatest steric hindrance in hydrocarbon molecules appears when t-alkyl groups are present as substituents. The mutual influence of a number of alkyl substituents in hydrocarbons has been observed by ^{1}H NMR spectroscopy (Table 7).

Table 7. Chemical shift of the protons in the t-butyl group [58].

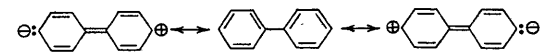
Compound	δ, p.p.m.	Compound	δ, p.p.m.
$(CH_3)_3C$—C$(CH_3)_3$	0.870	1,3-[$(CH_3)_3C]_2$—C_6H_4	1.31
$(CH_3)_3C$—H	0.905	1,4-[$(CH_3)_3C]_2$—C_6H_4	1.31
$(CH_3)_3C$—CH_3	0.927	1,2-[$(CH_3)_3C]_2$—C_6H_4	1.54
$(CH_3)_3C$—CH=CH_2	1.000	1,3,5-[$(CH_3)_3C]_3$—CH_3	1.34
$(CH_3)_3C$—C≡CH	1.20	1,2,4-[$(CH_3)_3C]_2$—C_6H_3	1.53
$(CH_3)_3$—C_6H_5	1.32	1,2,4,5-[$(CH_3)_3C]_4$—C_6H_2	1.48

4. Steric Hindrance to π,π- and σ,π Conjugation. Ultraviolet Absorption Spectra of Hydrocarbons

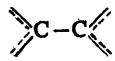
One of the main methods for the detection of steric hindrance in hydrocarbon molecules containing a π,π- or σ,π conjugated bond system consists in the investigation of their ultraviolet absorption spectra. The ultraviolet spectra of conjugated hydrocarbons depend to a considerable degree on the steric disposition of atoms in their molecules [59].

Theoretical studies by Hückel [60] and Pauling [61] and X-ray diffraction analysis established that a π,π conjugated system tends towards a distribution in one plane, since in this configuration the axes of the *p*-electronic orbitals are parallel and the orbitals overlap to the maximum extent.

The decrease of the mutual overlapping of *p* orbitals in a conjugated system when its coplanarity breaks down is shown in a change of the ultraviolet absorption spectra. These changes consist of a displacement of the *K* absorption bands towards shorter wavelengths with a simultaneous decrease of absorption intensity (ϵ_{max}). An example of this is provided by the ultraviolet absorption spectra of stilbene and dialkyl-substituted biphenyls [62]. Biphenyl, the molecule of which is coplanar owing to mesomeric forms,



absorbs much more intensely than *oo'*-dimethylbiphenyl (Fig. 1). The absorption due to the latter is very similar to that of toluene, which is evidence of a decrease of π,π conjugation via the central bond as the phenyl rings are displaced from coplanarity owing to the *oo'*-dimethyl groups. Binaphthyls [63] and 2,3-dialkyl-substituted buta-1,3-dienes [19] have similar ultraviolet spectra. The electronic spectrum of *αα'*-binaphthyl resembles that of naphthalene, while the spectrum of *ββ'*-binaphthyl reveals a strong conjugation between the naphthyl systems, that of *αβ*-binaphthyl being of an intermediate type. Thus the "peri-hydrogen atom" in naphthalene gives rise to fairly considerable steric hindrance to rotation about the

 bond in *αα'*-binaphthyl.

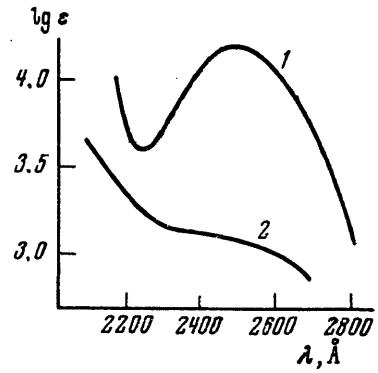
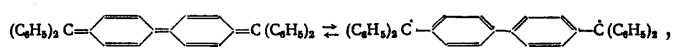


Figure 1. Ultraviolet absorption spectra (in ethanol): 1) biphenyl; 2) *oo'*-dimethylbiphenyl.

On the basis of the ultraviolet absorption spectra of methylated biphenyls, Suzuki [64] calculated the angle of φ between the planes of the benzene rings and found that the angle for the biphenyls in solution depends on the number of substituted *o*-positions. The relevant data are given in Table 8.

Koptyug et al. [65] showed that, in the ^{1}H NMR spectra of methylated biphenyls, the signals due to the protons of the methyl group in the *o*-positions are displaced to a lower field relative to the signals of the protons in the methyl groups occupying the *m*- and *p*-positions.

The steric hindrance to π,π conjugation in biphenyls promotes the stability of the corresponding free radicals [66,67]. Thus Chichibabin's hydrocarbon [68],



is a biradical only to the extent of 4%, but, when methyl groups are introduced into the *oo'*-positions of its biphenyl system, it exhibits the properties of a biradical to the extent of 100%:[69]

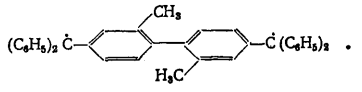
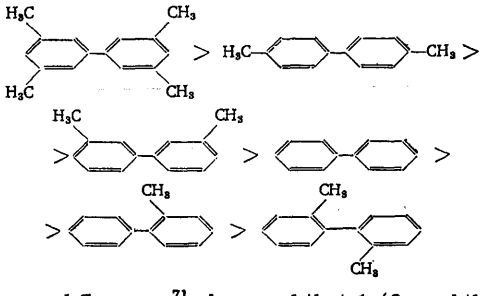


Table 8. The angle φ between the benzene rings in *o*-substituted biphenyls.

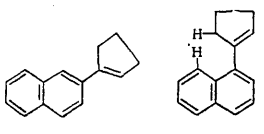
Substituents in positions				$\varphi°$
2	2'	6	6'	
H	H	H	H	20
CH_3	H	H	H	58
CH_3	CH_3	H	H	70
CH_3	CH_3	CH_3	CH_3	90

This implies that the mutually perpendicular (or nearly so) positions of the benzene rings, which arise owing to the *oo'*-dimethyl groups, are to a considerable degree responsible for the independence of the π electrons of these nuclei and of both unpaired electrons.

The steric hindrance to π,π conjugation in *oo'*-dimethyl derivatives of biphenyls has a significant influence on the stability of the molecular complexes of the methyl derivatives of biphenyl (donor) with trinitrobenzene (acceptor)[70]. It has been shown that the substitution of methyl groups in the *ortho*-positions in biphenyl, in contrast to the substitution in the *meta*- and *para*-positions, has an unfavourable effect on the stability of the complex, which diminishes in the following sequence:



Klemm and Sprague[71] observed that 1-(2-naphthyl)cycloalk-1-enes, particularly cyclopentene and cyclohexene derivatives, form with 2,4,7-trinitrofluorenone in acetic acid more stable complexes than those of 1-(1-naphthyl)-cycloalk-1-enes:



The low stability of the complexes formed by donors of the second type is due to the fact that the cycloalkene ring is displaced from the plane of the naphthalene ring system owing to steric hindrance caused by the peri-hydrogen.

Changes in the electronic absorption spectra analogous to those of alkyl-substituted biphenyls are observed for alkyl-substituted dienes and styrenes. In particular the absorption intensity of the *K* band in the spectra of dienes with the structure $R-CH=CH-CH=CH_2$ is higher than for dienes with "central depression": $CH_2=\underset{\displaystyle R}{\overset{\displaystyle |}{C}}-CH=CH_2$. On the other hand, it has been shown than an increase of the bulk of the group R in $CH_2=\underset{\displaystyle R}{\overset{\displaystyle |}{C}}-CH=CH_2$ leads to the breakdown of the coplanarity of the vinyl fragments and a decrease of the π,π conjugation (Table 9).

Table 9. Parameters of the ultraviolet absorption spectra of alkyl-substituted dienes.

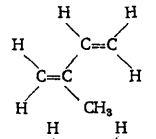
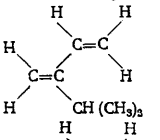
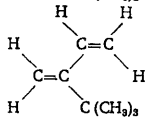
Compound	$\lambda(\varepsilon)$ in iso-octane, nm	$\vartheta°$
	223 (22100)	0
	223 (12000)	45
	224 (5400)	60

Table 9 shows that an increase of the size of group R increases the angle of deviation of the vinyl fragments from coplanarity (θ) and causes a corresponding decrease of the degree of conjugation in the $CH_2=CR-CH=CH_2$ molecule, reflected in a decrease of the absorption intensity.

The hindrance to π,π conjugation in diene molecules has a significant influence on the stability of their complexes with silver. It has been shown[73] that the stability of such complexes diminishes in the sequence buta-1,3-diene > 2-methylbuta-1,3-diene > 2,3-dimethylbuta-1,3-diene.

Apart from the steric hindrance to π,π conjugation, i.e. to electronic interaction between two or more multiple bonds, there is steric inhibition of σ,π conjugation in hydrocarbons. The electronic spectra of alkylbenzenes provide an example. The changes undergone by the electronic absorption spectrum of benzene as a result of the introduction of an alkyl group into the ring are due to a displacement towards the benzene ring of the electrons of the C–H bonds involving the α-carbon atom of the alkyl group, i.e. are a result of σ,π conjugation[74]. In the presence of steric hindrance in the molecule, the conjugation of the alkyl groups with the benzene ring is weakened; the absorption intensity diminishes and the electronic spectrum is displaced towards shorter wavelengths. On the other hand, a displacement of the spectrum towards longer wavelengths with increase of absorption intensity is evidence of an increase in the degree of conjugation of the system. It is interesting to note that the bathochromic shift of the characteristic absorption band and the increase of its intensity occur in the sequences *ortho*- < *meta*- < *para*- for dialkylbenzenes (Fig. 2), *cis*- < *trans*- for

olefins, and α- < β- for monoalkylnaphthalenes, in agreement with the decrease of the steric hindrance in these molecules.

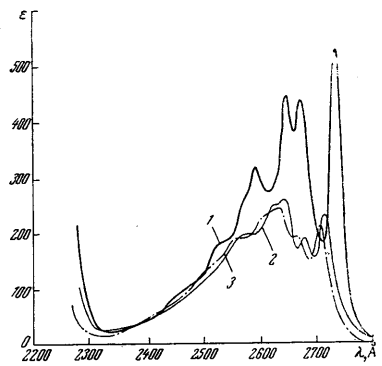


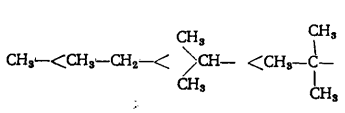
Figure 2. Ultraviolet absorption spectra of cymenes: 1) *p*-cymene; 2) *m*-cymene; 3) *o*-cymene.

Steric hindrance, which inhibits conjugation (electron delocalisation) in hydrocarbons, affects primarily the rates of their chemical reactions. Thus, in a study of the chlorination of alkylbiphenyl ring systems with molecular chlorine, de la Mare [75] established that the methyl groups in the *para*- and *meta*-positions increase sharply the rate of reaction. The chlorination rate constant for the *oo'*-dimethyl derivative of biphenyl, where there is steric hindrance to the electron shift (conjugation), is smaller by a factor of 16 compared with that for 4,4'-dimethylbiphenyl. A similar situation is observed in hydrocarbons with steric hindrance to σ,π conjugation. It has been found that the rate of abstraction by the trichloromethyl-radical of the α-hydrogen atom in the isopropyl group of *o*-cymene, in which there is steric hindrance to σ,π conjugation, is lower than in *p*- and *m*-cymenes, where there is no steric hindrance (Table 10). The same relative reactivities of cymenes have been observed in liquid-phase autoxidation [77].

Table 10. Relative rates of reaction of cymenes with the trichloromethyl radical.

Hydrocarbon	Relative rates
o-Cymene	0.44
m-Cymene	2.3
p-Cymene	2.5

According to the literature [2,79], steric hindrance increases with the degree of branching of the alkyl groups in the sequence:



and the bulk of the alkyl group as a whole does not have a steric effect as marked as branching at its α-carbon atom. The finding that small alkyl groups with maximum branching at the α-carbon atom give rise to more pronounced steric hindrance than bulkier alkyl groups but without such branching was already pointed out in earlier investigations. Alkyl groups can be arranged in the following sequence in terms of decreasing capacity for steric repulsion:

$$(CH_3)_3C- > (CH_3)_3C-CH_2- > (CH_3)_3C-CH_2-CH_2- \quad .$$

III. STERIC HINDRANCE IN THE SYNTHESIS OF HYDROCARBONS

1. Synthesis of Alkylbenzenes and Alkylnaphthalenes

Alkylation is one of the commonest methods of synthesis of hydrocarbons [80]. The addition of alkyl groups to the aromatic ring in the presence of acid catalysts takes place in accordance with the directing rules for the benzene ring [81,82]. Thus when toluene is alkylated with primary and secondary alcohols and alkyl halides in the presence of acid catalysts, the main products are *para*- and *ortho*-alkyltoluenes. Alkylation of toluene with tertiary alcohols and t-alkyl halides leads to the formation of *para*-t-alkyltoluene with only a low content of the *meta*-isomer. *p*-Xylene is not alkylated with t-butyl alcohol and t-butyl halides.

Baur [83], who alkylated *m*-xylene with t-butyl bromide in the presence of $AlCl_3$, and Noelting [84], who butylated the same hydrocarbon with t-butyl alcohol using sulphuric acid as a catalyst, obtained the same product: 5-t-butyl-1,3-dimethylbenzene.

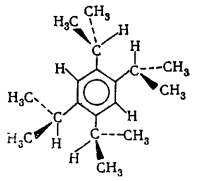
Despite the fact that the distribution of electron density in the aromatic ring of *m*-xylene (the concerted orientation of the two methyl groups) favours 1,3,4-substitution, steric hindrance to this mode of alkylation results in the formation of the symmetrical (anomalous) 1,3,5-isomer. It has been shown [85-88] that the alkylation product does not undergo subsequent isomerisation under the above conditions, i.e. it is the primary product of the addition of the t-alkyl cation. It is noteworthy that such substitution does not depend on the nature of the acid catalyst and takes place only with the t-butyl group, while the introduction of the s-butyl group into *m*-xylene under the influence of sulphuric acid and boron trifluoride gives rise to the formation of the 1,3,4-isomer.

The use of accurate modern analytical methods (capillary gas–liquid chromatography combined with infrared spectroscopy) in the study of the composition of the products of the alkylation of toluene and xylenes with various tertiary alcohols and alkyl halides in the presence of acid catalysts led to the demonstration of the absence or an extremely low content of *o*-t-alkyltoluenes and *o*-t-alkylxylenes [89-101].

It follows from the literature data [102] on this problem that the main reason for the anomalous behaviour of the t-alkyl group in alkylation reactions in the presence of acid catalysts is its bulk, which gives rise to considerable steric hindrance. However, on the basis of the bulk of the alkyl group alone, it is difficult to explain why, for example, the cyclohexyl group, which is bulkier than the t-butyl group, enters fairly readily the *ortho*-position relative to the methyl group [103].

Analysis of the structures of the *o*-dialkylbenzenes obtained by alkylation in the presence of acid catalysts showed that they contain at least one α-C–H bond in

adjacent alkyl groups. Owing to mutual repulsion, branched adjacent alkyl groups are oriented in such a way that their nearest interacting components become the protons of the α-C–H bonds, which is clearly illustrated by tetraisopropylbenzene as a model:



The minimum repulsion energy corresponds to this distribution of alkyl groups. In contrast to methyl, ethyl, and isopropyl groups, there is no similar possibility of orientation of the t-butyl group, so that its steric repulsion increases sharply [104]. A similar conclusion follows from an examination of the reaction mechanism and the geometry of the transition state.

The mechanism of the alkylation of aromatic hydrocarbons with olefins is known to involve electrophilic aromatic substitution. The mechanism of the alkylation with olefins in the presence of acid catalysts is usually treated on the basis of the hypothesis of the intermediate formation of active species: either alkyl derivatives of the acid or carbonium ions.

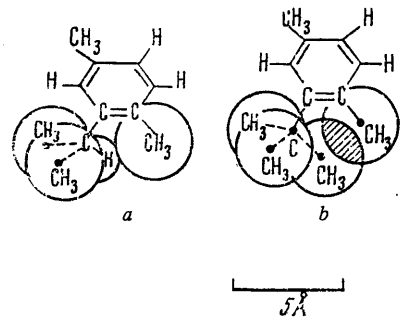
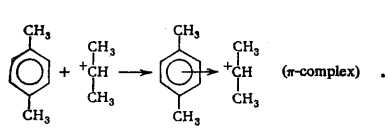
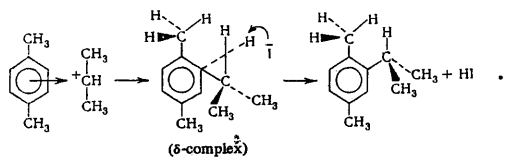


Figure 3. Molecular models: *a*) *o*-isopropyl-*p*-xylene; *b*) *o*-t-butyl-*p*-xylene.

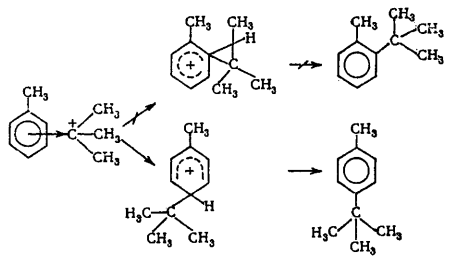
At the present time the carbonium ion theory of acid-catalysed alkylation reactions is the most popular. The existence of alkyl cations in strong acid solutions has been demonstrated by spectroscopic methods in many investigations [105,106]. Consequently alkylation of *p*-xylene takes place as follows:



The π complex rearranges to a σ complex which in the case of *ortho*-alkylation can be represented schematically as follows:



The scheme shows that the isopropyl group in the σ-complex transition state is oriented in such a way that the nearest interacting components of this group and of the methyl are the protons of the α-C–H bonds, which corresponds to the minimum repulsion energy between the *ortho*-alkyl groups. Evidently this state corresponds to the addition of any primary or secondary alkyl group. However, when a t-butyl group is introduced, then in the σ-complex transition state and in the resulting *o*-dialkylbenzene the steric repulsion effect increases sharply, as shown clearly in Fig. 3. Tending to reduce its potential energy to a minimum, the sterically strained molecule decreases the repulsive force by increasing the distance between the alkyl groups. Therefore, when the t-butyl group adds to toluene and *m*-xylene, the *ortho*-isomer is not formed:



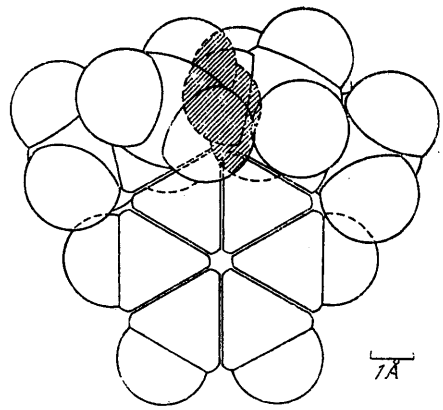


Figure 4. Molecular model of *o*-di-t-butylbenzene.

However, *o*-t-butyltoluene and 4-t-butyl-*m*-xylene were obtained by organomagnesium synthesis. Moreover, the t-butyl group was introduced into the ring by this method in the *ortho*-position relative to another t-butyl group [107]. Models for *o*-di-t-butylbenzene show marked overlapping of the van der Waals spheres of the alkyl groups (Fig. 4). The chemical properties of 1,2-di-t-butylbenzene have been investigated in detail. It is interesting to note that, on ultraviolet irradiation, it gives a mixture of the *m*- and *p*-isomers (20 and 80% respectively), which are more resistant to light; *o*-t-butyltoluene also isomerises under these conditions, but much more slowly.

Bulky adjacent groups undergoing a steric interaction with one another can actually alter the steric structure of the hydrocarbon. This has been confirmed by the finding that in 1,2,4,5-tetra-t-butylbenzene the ring is distorted so much that the boat conformation was assigned to it [108]. On irradiation with ultraviolet light, the compound isomerises to a derivative of "Dewar" benzene.

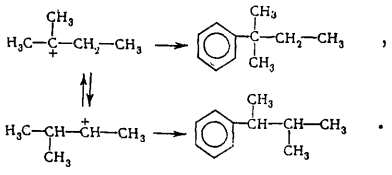
Thus in sterically hindered *o*-dialkylbenzene there is a strain in the π-electron system of the aromatic ring similar to the strain of the π-electron system of the double bond in strained *cis*-dialkylethylenes.

Steric hindrance due to t-alkyl groups arises also in the alkylation of naphthalene. However, here the hindrance is not caused by an adjacent alkyl group but by the "peri-hydrogen", which hinders the introduction of t-alkyl groups into the α-position of the naphthalene ring. Whereas t-butylmagnesium bromide reacts with bromobenzene, the reaction with α-bromonaphthalene does not occur [2]. The alkylation of naphthalene with isobutene in the presence of acid catalysts takes place anomalously, like the alkylation of toluene: only β-t-butylnaphthalene is obtained [109]. However, s-alkyl groups (isopropyl [110,111] and cyclohexyl [112,113] groups) enter the α-position of naphthalene fairly readily owing to the presence in these groups of the α-C–H bond, which permits a [favourable] orientation of the alkyl group relative to the "peri-hydrogen".

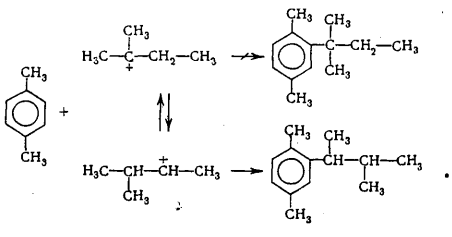
2. Anomalous Isomerisation of t-Alkyl Groups in the Alkylation of Hydrocarbons

Until recently, it was regarded as generally accepted and demonstrated that, in the alkylation of an aromatic ring with t-butyl halides, tertiary alcohols, and iso-olefins, there is no rearrangement of the resulting tertiary carbonium ions; the tertiary carbonium ion formed alkylates the aromatic ring with formation of t-alkylbenzenes [114].

However, it has been noted in a number of studies [115,116] that in the alkylation of benzenes secondary alkyl derivatives are formed together with tertiary derivatives. This is indicated, in particular, by the formation of a mixture of secondary and tertiary (main product) pentylbenzenes on alkylation of benzene with isopentyl chloride and pentenes in the presence of aluminium chloride at 0°C: [115,120]



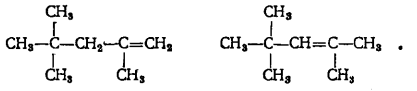
The equilibrium between the tertiary and secondary ions can be displaced towards the latter species under the influence of steric hindrance. Thus Friedman and Morritz [117], who alkylated *p*-xylene with isopentenes in the presence of BF_3 and $AlCl_3$ at 0°C, observed the formation (in yields up to 40%) of s-pentyl derivatives exclusively, which was confirmed by a careful analysis using infrared and mass spectrometry. They suggested that, when alkylation by tertiary ions (in the *ortho*-position of *p*-xylene) is hindered, the less sterically hindered secondary ions, in equilibrium with the tertiary ions, enter the ring:



3. Oligomerisation and Polymerisation of Alkyl- and Aryl-substituted Olefins

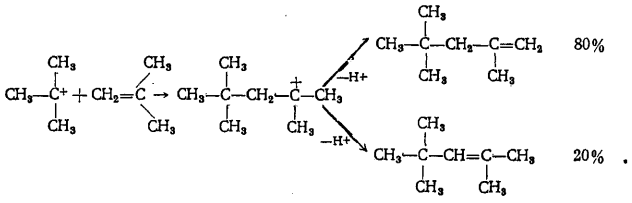
The first systematic studies on the reactivity of ethylene derivatives in the oligomerisation reaction were carried out by Lebedev and Filonenko [118], who observed that at room temperature in the presence of floridin only asymmetric di- and tri-substituted ethylene derivatives are polymerised. Further study of this problem and analysis of the accumulated experimental data enabled Korshak and coworkers [119,120] to conclude that steric effects as well as electron factors play an important role in the olefin polymerisation process.

The effect of steric hindrance is usually shown in two ways; (1) the rate of oligomerisation of olefins decreases with increasing number and bulk of substituents at the double bond and (2) the isomeric composition of the reaction products changes. In 1873 Butlerov [121] described the dimerisation of isobutene under the influence of sulphuric acid, which results in the formation of di-isobutene. The structure of di-isobutene was the subject of numerous investigations [122–125] which established accurately that this hydrocarbon is a mixture of two isomers:



The isomer with the double bond in the α-position predominates in the mixture.

On the basis of modern concepts, the dimerisation of isobutene may be represented by the following scheme:



The t-butyl cation adds to the isobutene molecule and forms a C_8 carbonium cation. The abstraction of a proton from the latter leads to the formation of two isomeric olefins in proportions of 4 : 1. The transition state in the reaction involving the abstraction of a proton from the carbonium cation contains a partial double bond (Fig. 5) stabilised by the hyperconjugation of the alkyl substituents with the electrons of the incipient π bond [126]. However, owing to steric hindrance, the formation of the β-olefin in the transition state is energetically unfavourable, as shown by the shaded part of the van der Waals spheres in the models (Fig. 5). Therefore the energetically more favourable α-olefin, in which there is no steric hindrance, is formed preferentially.

Similar steric hindrance in the transition state determines the composition of iso-olefins in the dimerisation of more complex hydrocarbons also, for example isohexenes. Thus a study of the oligomerisation of two isohexenes—2-methylpent-1-ene and 2-methylpent-2-ene [3,127]—revealed the preferential formation of isododecenes the double bond of which is remote from the quaternary carbon atom, i.e. 4,6,6-trimethylnon-3-ene and 3-ethyl-2,4,4-trimethylhept-1-ene and not 4,6,6-trimethylnon-4-ene and 3-ethyl-2,4,4-trimethylhept-2-ene (Fig. 6).

The relative contents of isododecenes with different hydrocarbon frameworks in the reaction products are determined by the concentrations of the individual hexenes in the mixture and their capacity for interaction with the

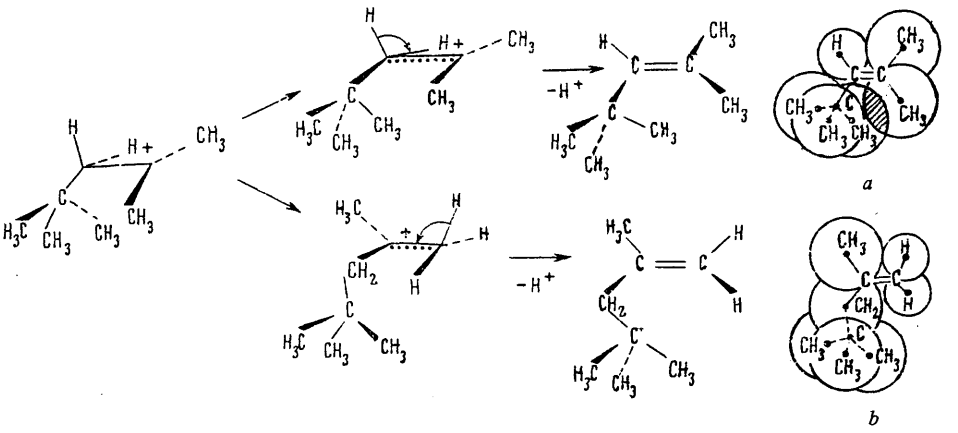


Figure 5. A three-dimensional scheme illustrating the formation of di-isobutenes and their models: *a*) 2,4,4-trimethylpent-2-ene; *b*) 2,4,4-trimethylpent-1-ene.

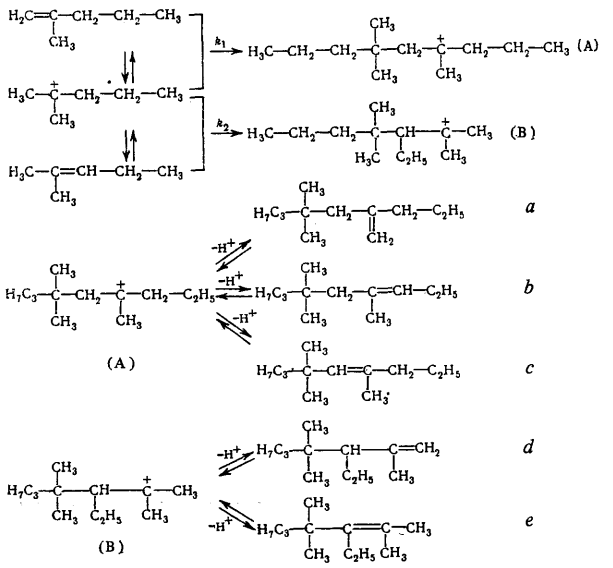


Figure 6. The mechanism of the dimerisation of isohexenes [127,128].

t-hexyl cation. It has been shown [127] that the rate of electrophilic addition of the t-hexyl cation to 2-methylpent-1-ene is five times faster than the rate of addition to 2-methylpent-2-ene, which can be explained by electronic and steric effects. The relative proportions of isododecenes with the same carbon framework but differing in the position of the double bond depend on their thermodynamic stabilities and the relative rates of abstraction of protons from different alkyl groups in the 4,6,6-trimethyl-4-nonyl cation (A) and 3-ethyl-2,4,4-trimethyl-2-heptyl cation (B).

The influence of structural factors on the rate and mode of reactions of carbonium ions has been the subject of controversy [129] and in the general case may be determined both by steric [130] and electronic effects [131,132]. A graphical representation of isododecene molecules (Fig. 7) with the bond lengths, valence angles, and actual radii of the substituents drawn to scale [59] shows that steric hindrance has a distinct effect on the structures of various isododecenes (on the basis of the overlapping of the spheres of groups not directly linked by valence bonds) (Fig. 7). Maximum steric hindrance, which occurs in the β-isododecene molecule and hence also in the transition state, results in the formation of α-isododecene as the main product of the abstraction of a proton from the 3-ethyl-2,4,4-trimethyl-2-heptyl cation (B). The insignificant formation of the β-olefin is caused by its lower thermodynamic stability owing to the marked steric hindrance arising as a result of the repulsion between the *cis*-methyl groups at the unsaturated and quaternary carbon atoms. The preferential formation of isododecene (*b*) compared with the olefin (*c*) on deprotonation of the 4,6,6-trimethyl-4-nonyl cation (A) can be explained similarly.

The literature and the present authors' experimental data [3] in Table 11 for the compositions of the oligomers should be regarded as confirmation of the hypothesis concerning the increasing role of steric effects in the formation of α-olefins on passing from the relatively low-molecular-weight C_6 hydrocarbons to the higher C_{12} hydrocarbons.

The introduction of a t-alkyl group in the β-position relative to the positively charged tertiary carbon atom increases sharply the yield of the α-olefin (Table 10). This is because, owing to the "cisoid repulsion strain" in the transition state, the formation of the β-olefin becomes energetically less favourable than that of the α-olefin, i.e. the energies of the σ,π conjugation of the alkyl substituents with the double bond of the olefin formed is no longer sufficient to overcome the steric hindrance.

The preferential formation of α-olefins, observed in the oligomerisation of olefins in the presence of acid catalysts, occurs [also] in the dehydration of alcohols and in the solvolysis of alkyl halides [139].

Thus steric factors are dominant in all elimination reactions leading to olefins if alkyl groups, at least one of which is tertiary, are present in the transition state in the *cis*-position relative to the double bond.

Molecular steric hindrance plays an important role in the polymerisation of olefins. Korshak [133] showed that the capacity for polymerisation of alkyl- and aryl-substituted olefins depends to a considerable degree on the screening of the double bond by substituents, i.e. on the steric hindrance caused by them. The influence of substituents is directly proportional to their bulk and their number.

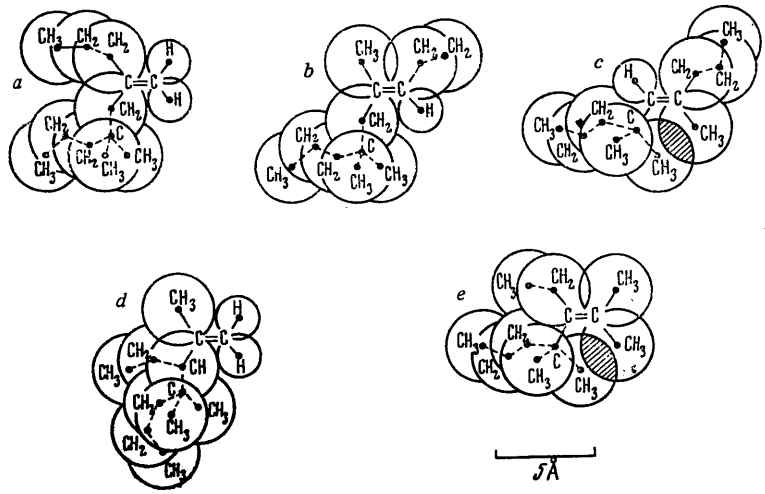
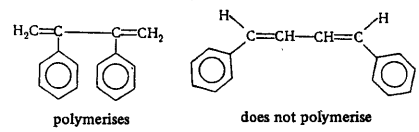


Figure 7. Molecular models of isododecenes: *a*) 4,4-dimethyl-2-propylhept-1-ene; *b*) 4,6,6-trimethylnon-3-ene; *c*) 4,6,6-trimethylnon-4-ene; *d*) 3-ethyl-2,4,4-trimethylhept-1-ene; *e*) 3-ethyl-2,4,4-trimethylhept-2-ene.

Table 11. The structures of carbonium cations and the concentrations of iso-olefins obtained from them.

α-Olefins	Wt. %	Carbonium cation	β-Olefin	Wt.%
$CH_2{=}C(CH_3){-}CH_2{-}CH_2{-}CH_3$	16	$CH_3{-}C^+(CH_3){-}CH_2{-}CH_2{-}CH_3$	$CH_3{-}C(CH_3){=}CH{-}CH_2{-}CH_3$	84
$CH_2{=}C(CH_3){-}CH_2{-}CH(CH_3){-}CH_3$	18	$CH_3{-}C^+(CH_3){-}CH_2{-}CH(CH_3){-}CH_3$	$CH_3{-}C(CH_3){=}CH{-}CH(CH_3){-}CH_3$	82
$CH_2{=}C(CH_3){-}CH_2{-}C(CH_3)_2{-}CH_3$	82	$CH_3{-}C^+(CH_3){-}CH_2{-}C(CH_3)_2{-}CH_3$	$CH_3{-}C(CH_3){=}CH{-}C(CH_3)_2{-}CH_3$	18
$CH_3{-}C(CH_3){=}CH{-}C(CH_3)_2{-}CH_3$	83	$CH_3{-}C^+(CH_3){-}CH(CH_3){-}C(CH_3)_2{-}CH_3$	$CH_3{-}C(CH_3){=}C(CH_3){-}C(CH_3)_2{-}CH_3$	17
$CH_2{=}C(CH_3){-}CH(CH_3){-}C(CH_3)(C_2H_5){-}C_3H_7$	90	$CH_3{-}C^+(CH_3){-}CH(CH_3){-}C(CH_3)(C_2H_5){-}C_3H_7$	$CH_3{-}C(CH_3){=}C(CH_3){-}C(CH_3)(C_2H_5){-}C_3H_7$	10

The concepts concerning steric hindrance developed by Korshak were confirmed also in the polymerisation of branched diene hydrocarbons. According to the mechanism established by Lebedev[134,137], butadiene polymerises with formation of carbon–carbon bonds in the 1- and 4-positions. Thus when the 1- and 4-carbon atoms are screened, polymerisation does not occur. On the other hand, if the 2- and 3-carbon atoms are screened, hindrance to polymerisation does not arise, which has been confirmed experimentally:



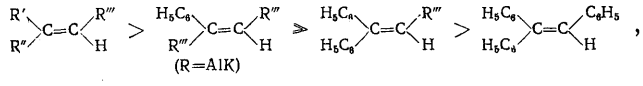
It is noteworthy that, apart from the steric factor, the conjugation effect apparently plays an important role in this case. In 1,4-diphenyl-substituted butadienes it is much more pronounced than in 2,3-diphenyl derivatives, since in the latter the phenyl groups are not included in the conjugated system of the diene.

Steric hindrance in the hydrocarbon molecule does not only retard but in some cases actually accelerates the radical polymerisation of olefins. Thus it has been established that the rate of polymerisation of α-vinylnaphthalene is higher[135] by a factor of 2.5 than the rate of polymerisation of styrene. This can be explained as follows: the vinyl group of α-vinylnaphthalene is displaced from the plane of the naphthalene ring system owing to the steric hindrance due to the "peri-hydrogen", which leads to a decrease of its conjugation with the naphthalene ring system. According to Bagdasar'yan's theory[136], a less conjugated olefin should give rise to a more reactive radical, which in fact is the reason for the higher rate of polymerisation. This leads to the following practical conclusion: in order to obtain the most reactive hydrocarbon monomers, it is necessary to synthesise hydrocarbons with a strained double bond.

4. Synthesis of Branched Alkanes

The screening of the double bonds by hydrocarbon substituents affects not only the polymerisation but also the

hydrogenation of branched olefins to alkanes. As early as the 1920's, Lebedev and coworkers[138] established that ethylene derivatives substituted to different extents are hydrogenated in different ways. The compounds R–CH=CH_2 are hydrogenated at the highest rate and CR_2=CR_2 at the lowest. This has been shown particularly convincingly by Kazanskii and coworkers[139,140], who established that in the presence of platinum black the rate of hydrogenation decreases in the following sequence:



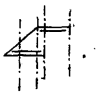
i.e. olefins with the double bond screened to a greater extent are hydrogenated at a lower rate. The rate of dehydrocyclisation of olefins is influenced more by their steric structure than by the position of the double bond[141]. The effect of the branching of the carbon framework of olefins on the yield of aromatic compounds has not in fact been investigated.

The first attempts to obtain by the Wurtz method fully methylated derivatives of higher ethane homologues were unsuccessful[142]. In general the synthesis of hexa-alkylethanes by the dimerisation of two tertiary alkyl groups is extremely difficult. The simplest analogue—hexamethylethane—was obtained from t-butyl chloride and sodium over a period of 10 days in a yield of 10%. In a number of studies[143,144], where t-alkyl halides were used in the Wurtz reaction, extremely low yields of branched alkanes were noted. Somewhat higher yields of these compounds are obtained in the organomagnesium synthesis. Therefore, for a successful synthesis of branched alkanes, it was necessary to seek ways whereby the effect of steric hindrance could be reduced to some extent[2].

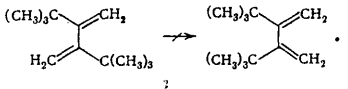
The steric hindrance in iso-olefin molecules promotes their decomposition on cracking. Thus Nazarov[142] established that the asymmetric di-t-butylethylene is readily cleaved at the site of addition of the tertiary group into lower olefins on distillation with traces of 2-bromonaphthalene-4-sulphonic acid. However, when one of the t-alkyl groups is replaced by a phenyl group, the resulting asymmetric t-alkylphenylethylenes become stable and are not cleaved even above 300°C.

5. Diels–Alder Synthesis

The Diels–Alder synthesis is a type of condensation in which a diene reacts with a dienophile in a coplanar cisoid conformation:



Naturally dienes in which such cisoid conformation of the double bonds does not arise under the experimental conditions owing to steric hindrance cannot enter into the Diels–Alder synthesis[145]. Thus Backer and Strating[146,147] showed that 2-t-butylbutadiene enters into the Diels–Alder synthesis normally, while 2,3-di-t-butylbutadiene does not react at all because it cannot assume the cisoid conformation necessary for the reaction, owing to the steric hindrance by the adjacent t-butyl groups[148]:



On the other hand, 1,3-di-t-butylbutadiene, in which the t-butyl groups are further apart and do not give rise to a steric effect, enters fairly readily[149,150] into Diels–Alder reactions. In general, if the formation of a coplanar cisoid conformation of the diene is interferred with by steric hindrance, the Diels–Alder synthesis as a rule takes place with difficulty and with low yields.

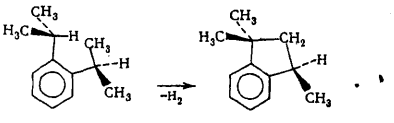
Table 12. The yield of indene in the cracking of cymenes (%).

Initial cymene	Indene
o-Cymene	3.6
m-Cymene	0
p-Cymene	0

6. The Formation of Indane–indene Structures

A characteristic feature of *o*-dialkyl derivatives of benzene is the formation of indene structures[151] (Table 12) on cracking.

The use of catalysts based on iron(III) oxide or aluminium oxide for the cracking of *o*-cymene increases the yield of indene. In the cracking of *o*-ethyltoluene, the yield of indene reaches 23%. Cyclisation of alkyl substituents as a result of their steric proximity with formation of indane derivatives was noted in the alkylation of isopropylbenzene with propene in the presence of aluminium chloride[152] according to the following mechanism:



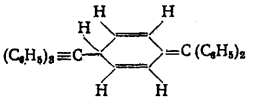
7. Dissociation of Hexa-arylethanes. The Structure of the Gomberg Hydrocarbon

In 1900 Gomberg[153] discovered the first free radical, which had an enormous influence on the further development of theory and practice in the field of organic free radicals. Gomberg obtained a free radical by treating chlorotriphenylmethane with metals (zinc, copper, and silver).

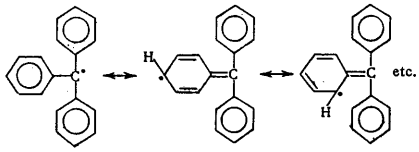
Numerous investigations led to the belief (Wieland, 1909) that chlorotriphenylmethane initially yields hexaphenylethane, which in benzene solutions consists of an equilibrium mixture of hexaphenylethane and triphenylmethyl radicals, the former predominating.

Markovnikov and Chichibabin[154] believed that the Gomberg hydrocarbon is not true hexaphenylethane but is merely identical with it [sic!].

Interesting studies on the dimer of the triphenylmethyl radical were published in 1968.[155–158] ^{1}H NMR and ultraviolet spectroscopy showed that the product of the association of the triphenylmethyl radicals obtained from chlorotriphenylmethane and silver is a hydrocarbon with the structure



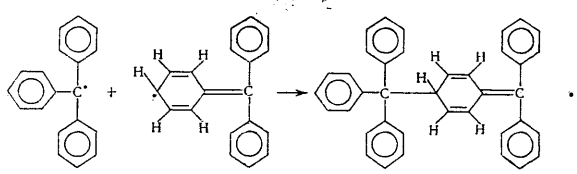
the formation of which can be understood bearing in mind that the triphenylmethyl radical can have several resonance forms:



The formation of hexaphenylethane on recombination of the classical form is difficult due to steric hindrance: under the influence of the *ortho*-hydrogen atoms, each phenyl ring is extended relative to the axis joining it to the central carbon atom which results in a propellor structure [159] in which the unpaired electron of the radical is screened by the *ortho*-hydrogen atoms.

Such radicals cannot approach one another to a distance sufficient for the formation of a C–C bond. It is interesting to note that at one time Gomberg also rejected the possibility of the dimerisation of triphenylmethyl radicals to hexaphenylethane. He wrote "...if the three valences of the carbon atom are occupied by three phenyl groups, it is difficult and probably actually impossible to introduce a complex species such as triphenylmethyl" [153]. Gomberg suggested that the association of triphenylmethyl radicals does not take place via the combination of the main (ethane) valences but in some other way.

On the basis of the above structure of the dimer of the triphenylmethyl radical, its formation actually takes place according to the following mechanism:



It should be noted that this structure of the triphenylmethyl radical dimer was proposed as early as 1905 by Jacobson [160], but, in view of the experimental difficulties involved in proving it, it remained neglected.

Thus the steric hindrance arising in the molecule play an important role here. As a result, hexaphenylmethane has still not been synthesised and [therefore] the field of triphenylmethane compounds should be thoroughly re-examined.

REFERENCES

1. "Novye Neftekhimicheskie Protsessy i Perspektivy Razvitiya Neftekhimii" (New Petrochemical Processes and Prospects for the Development of Petrochemistry), from the Proceedings of the Seventh World Petroleum Congress in Mexico, Izd. Khimiya, Moscow, 1970.
2. A. D. Petrov, "Khimiya Motornykh Topliv" (The Chemistry of Motor Fuels), Izd. Akad. Nauk SSSR, Moscow, 1953, p. 26.
3. V. V. Voronenkov, A. N. Vinogradov, and V. A. Belyaev, Zhur. Org. Khim., 6, 1976 (1970).
4. Yu. G. Osokin, S. I. Kryukov, and V. V. Voronenkov, Neftekhimiya, 11, 630 (1971); Yu. G. Osokin, Neftekhimiya, 7, 871 (1967).
5. C. A. Thomas, M. B. Moshier, H. E. Morris, and R. W. Moshier, "Anhydrous Aluminium Chloride in Organic Chemistry" (Translated into Russian), Inostr. Lit., Moscow, 1949.
6. A. L. Petrov and E. A. Chernyshov, Uspekhi Khim., 22, 1188 (1953).
7. R. Ya. Levina and V. R. Skvarchenko, Uspekhi Khim., 18, 515 (1949).
8. F. Asinger, "Chemie und Technologie der Monoolefine" (Translated into Russian), Gostoptekhizdat, 1960.
9. W. G. Dauben and K. S. Pitzer, in "Steric Effects in Organic Chemistry" (Edited by M. F. Newman) (Translated into Russian), Inostr. Lit., Moscow, 1960.
10. O. V. Bragin and A. L. Liberman, Uspekhi Khim., 39, 2122 (1970) [Russ. Chem. Rev., No. 12 (1970)].
11. San-Ichiro Mizushima, "Structure of Molecules and Internal Rotation" (Translated into Russian), Inostr. Lit., Moscow, 1957.
12. E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis" (Translated into Russian), Izd. Mir, Moscow, 1969.
13. E. L. Eliel, "Stereochemistry of Carbon Compounds" (Translated into Russian), Izd. Mir, Moscow, 1969.
14. L. V. Vilkov and V. S. Mastryukov, Zhur. Strukt. Khim., 8, 595 (1967).
15. A. A. Bothner-By, C. Naar-Colin, and H. Günther, J. Amer. Chem. Soc., 83, 231 (1961); 84, 2748 (1962).
16. N. L. Allinger, J. A. Hirsch, M. A. Miller, and I. J. Tyminski, J. Amer. Chem. Soc., 90. 5773 (1968).
17. Yu. G. Osokin, Candidate's Thesis, The Technological Institute, Yaroslavl, 1970.
18. Yu. G. Osokin, V. Sh. Fel'dblyum, V. S. Dzyuba, M. E. Basner, and S. I. Kryukov, Zhur. Org. Khim., 6, 1357 (1970).
19. A. F. Moskvin, Candidate's Thesis, INKhS, Moscow, 1970.
20. Al. A. Petrov, "Khimiya Naftenov" (The Chemistry of Naphthenes), Izd. Nauka, Moscow, 1971.
21. D. Barton, Symposium, "Perspektivy Razvitiya Organicheskoi Khimii" (Horizons in Organic Chemistry) (Translated into Russian), Inostr. Lit., Moscow, 1959.
22. I. N. Nazarov and L. G. Bergel'son, Uspekhi Khim., 26, 3 (1957).
23. Ya. L. Gol'dfarb and L. I. Belen'kii, Uspekhi Khim., 29, 470 (1960) [Russ. Chem. Rev., No. 4 (1960)].
24. H. C. Allen and E. K. Plyler, J. Chem. Phys., 31, 1062 (1959).
25. B. D. Lide and D. E. Mann, J. Chem. Phys., 27, 868 (1957).
26. L. V. Vilkov, N. I. Sadova, and Yu. I. Zil'berg, Zhur. Strukt. Khim., 8, 528 (1967).
27. L. V. Vilkov and N. I. Sadova, Dokl. Akad. Nauk SSSR, 162, 565 (1965).
28. A. I. Kitaigorodskii, Dokl. Akad. Nauk SSSR, 137, 116 (1961).
29. V. G. Dashevskii, Zhur. Strukt. Khim., 9, 29 (1968).
30. L. A. Chugaev, "Izbrannye Trudy" (Selected Works), Izd. Akad. Nauk SSSR, Moscow, 1962, Vol. III, pp. 25, 52.
31. J. Meisenheimer, Ber., 60, 1425 (1927).
32. W. H. Mills, Chem. Ind. (London), 45, 884, 905 (1926).
33. E. Muller, "Neuere Anschauungen der organischen Chemie" (Translated into Russian), Inostr. Lit., Moscow, 1960.
34. J. G. Cadogan, D. H. Hey, and G. H. Williams, J. Chem. Soc., 3352 (1954).
35. S. S. Batsanov, "Strukturnaya Refraktometriya" (Structural Refractometry), Izd. Moskov. Gos. Univ., Moscow, 1959.

36. V.V.Voronenkov, Neftekhimiya, 8, 581 (1968).
37. W.Hückel, "Theoretische Grundlagen der organische Chemie" (Translated into Russian), ONTI, Moscow, 1936, Vol. 2.
38. L.R.Avoyan, Yu.T.Struchkov, and V.G.Dashevskii, Zhur.Strukt.Khim., 7, 289 (1966).
39. A.Streitwieser and J.H.Hammons, in "Novye Problemy Fizicheskoi Organicheskoi Khimii" (New Problems in Physical Organic Chemistry) (Translated into Russian), Izd.Mir, Moscow, 1962, p. 21.
40. A.Werner, "Lehrbuch der Stereochemie", Jena, 1904, p. 219.
41. V.M.Tatevskii, "Khimicheskoe Stroenie Uglevodorodov i Zakonomernosti Ikh Fiziko-khimicheskikh Svoistv" (Chemical Structure of Hydrocarbons and Regularities in Their Physicochemical Properties), Izd.Moskov.Gos.Univ., Moscow, 1953.
42. H.G.Hecht and B.L.Victor, J.Amer.Chem.Soc., 90, 3333 (1968).
43. N.S.Zefirov and V.I.Sokolov, Uspekhi Khim., 36, 243 (1967) [Russ.Chem.Rev., No. 2 (1967)].
44. Yu.G.Mamedaliev and Sh.T.Akhundov, Uspekhi Khim., 23, 876 (1954).
45. S.Goldschmidt, "Stereochemie" (Translated into Russian), Goskhimizdat, Leningrad–Moscow, 1940, p. 125.
46. K.Auwers, Annalen, 420, 92 (1920).
47. B.A.Kazanskii and M.Yu.Lukina, Dokl.Akad.Nauk SSSR, 65, 693 (1949).
48. A.L.Liberman, T.V.Lapshina, and B.A.Kazanskii, Dokl.Akad.Nauk SSSR, 107, 93 (1956).
49. B.A.Kazanskii, A.L.Liberman, N.I.Tyun'kina, and I.N.Kuznetsova, Dokl.Akad.Nauk SSSR, 122, 1025 (1958).
50. B.A.Kazanskii, Dokl.Akad.Nauk SSSR, 134, 93 (1960).
51. A.L.Liberman and N.I.Tyun'kina, Neftekhimiya, 3, 828 (1963).
52. A.L.Liberman and B.M.Lerman, Neftekhimiya, 6, 520 (1968).
53. J.Brühl, Ber., 40, 878 (1907).
54. J.Brühl, Ber., 40, 1153 (1907).
55. V.V.Voronenkov and Yu.S.Musabekov, Neftekhimiya, 8, 713 (1968).
56. V.V.Voronenkov and Yu.S.Musabekov, Neftekhimiya, 10, 64 (1970).
57. V.S.Gutyrya, Zhur.Obshch.Khim., 7, 212 (1937).
58. W.O.Wilk, A.Allred, and B.A.Koven, J.Chem. Soc.(B), 565 (1969).
59. A.I.Kiprianov, G.G.Dyadyusha, and G.A. Mikhailenko, Uspekhi Khim., 35, 823 (1966) [Russ. Chem.Rev., No. 5 (1966)].
60. E.Hückel, Z.Elektrochem., 43, 752, 857 (1937).
61. L.Pauling and J.Scherman, J.Chem.Phys., 1, 679 (1933).
62. E.A.Braude and E.S.Waight, in "Uspekhi Stereokhimii" (Advances in Stereochemistry) (Translated into Russian), Goskhimizdat, Moscow, 1961, p.331.
63. A.Gillam and E.S.Stern, "Electronic Absorption Spectra of Physical Compounds" [An Introduction to Electronic Spectroscopy in Organic Chemistry?] (Translated into Russian), Inostr.Lit., Moscow, 1957, p. 337.
64. H.Suzuki, Bull.Chem.Soc.Japan, 32, 1340, 1350 (1959).
65. V.A.Koptyug, A.I.Rezvukhin, A.P.Krysin, and I.S.Isaev, Zhur.Strukt.Khim., 8, 622 (1967).
66. L.V.Koshkin and Yu.S.Musabekov, "Orcherki po Istorii Khimii" (An Outline of the History of Chemistry), Izd.Akad.Nauk SSSR, Moscow, 1963, p. 190.
67. L.V.Koshkin and Yu.S.Musabekov, "Vozniknovenie i Razvitie Predstavlenii ob Organicheskikh Svobodnykh Radikalakh" (The Origin and Development of Organic Free Radical Concepts), Izd.Nauka, Moscow, 1967, p. 124.
68. L.F.Fieser and M.Fieser, "Organic Chemistry" (Translated into Russian), Izd.Khimiya, 1966, Vol. 1, p. 413.
69. W.Theilacker and W.Ozegowski, Ber., 73, 33, 898 (1940).
70. L.J.Andrews and R.M.Keefer, "Molecular Complexes in Organic Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1967, p. 72.
71. H.L.Klemm and W.J.Spraque, J.Org.Chem., 19, 1464 (1954).
72. A.F.Moskvin, O.P.Yablonskii, V.V.Voronenkov, and Yu.Yu.Musabekov, "Materialy po Issledovaniyu Stroeniya Organicheskikh Soedinenii Fizicheskimi Metodami" (Studies on the Structure of Organic Compounds by Physical Methods), Kazan, 1971, p. 53.
73. M.A.Muhs and F.T.Weiss, J.Amer.Chem.Soc., 84, 4697 (1962).
74. M.M.Kusakov, I.A.Shimanko, and M.V.Shishkina, "Ul'trafioletovye Spektry Pogloshcheniya Aromaticheskikh Uglevodorodov" (Ultraviolet Absorption Spectra of Aromatic Hydrocarbons), Izd.Akad.Nauk SSSR, Moscow, 1963.
75. P.B.D.de la Mare, see Ref. 62, p. 526.
76. E.C.Kooyman and A.Strang, Rec.Trav.chim., 72, 329 (1953).
77. V.V.Voronenkov, A.N.Vinogradov, and V.A. Belyaev, Uspekhi Khim., 43, 1969 (1970) [Russ. Chem.Rev., No. 11 (1970)].
78. H.Kaufmann, Electrochemie, 25, 343 (1919).
79. A.N.Nesmeyanov and N.A.Nesmeyanov, "Nachalo Organicheskoi Khimii" (Principles of Organic Chemistry), Moscow, 1969, Vol. 1, p. 514.
80. A.V.Topchiev, S.V.Zavgorodnii, and V.G. Kryuchkov, "Reaktsiya Alkilirovniya Aromaticheskikh Soedinenii Olefinami" (Alkylation of Aromatic Compounds with Olefins), Izd.Akad.Nauk SSSR, Moscow, 1962.
81. C.Price, "Organic Reactions" (Translated into Russian), Inostr.Lit., Moscow, 1951.
82. V.N.Rodionov, V.N.Belov, and S.A.Kore, Trudy VNIISNDV (Pishchepromizdat), No. 1, 27 (1952).
83. A.Baur, Ber., 24, 2840 (1891).
84. E.Noelting, Ber., 25, 790 (1892).
85. D.Nightingale, H.D.Radford, and O.G. Shauholtzer, J.Amer.Chem.Soc., 64, 1662 (1942).
86. L.I.Smith and H.O.Perry, J.Amer.Chem.Soc., 61, 1411 (1939).
87. V.M.Rodionov, V.N.Belov, and S.A.Kore, Zhur. Obshch.Khim., 23, 1802 (1953).
88. R.Nakane, J.Amer.Chem.Soc., 88, 3011 (1966).
89. K.T.Serijan, H.F.Hipsher, and L.C.Gibbons, J.Amer.Chem.Soc., 71, 873 (1949).
90. R.H.Allen, J.Amer.Chem.Soc., 83, 2799 (1961).
91. M.J.Schlatter, J.Amer.Chem.Soc., 75, 361 (1953).
92. E.C.Kooyman, Rec.Trav.chim., 84, 1080 (1965).
93. G.A.Olah, M.W.Meyer, and N.A.Overchuk, J.Org. Chem., 29, 2310 (1964).
94. G.A.Olah, J.Amer.Chem.Soc., 86, 1060 (1964); 87, 5786 (1965).

95. B.V. Stolyarov, Symposium, "Sovremennye Problemy Organicheskoi Khimii" (Modern Problems in Organic Chemistry), Izd. Leningrad. Univ., 1969, p. 5.
96. M.I. Farberov and A.M. Kut'in, Neftekhimiya, 3, 313 (1965).
97. R.A. Sanford, J. Amer. Chem. Soc., 75, 6326 (1953).
98. B.S. Friedman, F.L. Morritz, C.J. Morrissey, and R. Koncos, J. Amer. Chem. Soc., 80, 5867 (1958).
99. A.V. Bondarenko and M.I. Farberov, Zhur. Prikl. Khim., 35, 1584 (1962).
100. M. Yu. Tikhvinskaya, A.V. Bondarenko, and M.I. Farberov, Neftekhimiya, 3, 548 (1963).
101. E.L. Styskin, A.V. Bondarenko, and M.I. Farberov, Neftekhimiya, 8, 404 (1968).
102. G.F. Hennion, A.J. Driesch, and P.L. Dee, J. Org. Chem., 17, 1102 (1952).
103. S.V. Zavgorodnii, I.A. Nasyr, I.I. Novikov, and E.V. Alisova, Ukrain. Khim. Zhur., 35, 374 (1969).
104. V.V. Voronenkov, V.I. Yulina, and E.A. Lazurin, Neftekhimiya, 11, 857 (1971).
105. D. Bethell and V. Gold, "Carbonium Ions: An Introduction" (Translated into Russian), Izd. Mir, 1970.
106. T.I. Temnikova, "Kurs Teoreticheskikh Osnov Organicheskoi Khimii" (A Course of the Theoretical Foundations of Organic Chemistry), Izd. Khimiya, 1968, p. 367.
107. A. Burgstahler, J. Amer. Chem. Soc., 86, 5281 (1964).
108. C. Hoogzand and W. Hübel, Tetrahedron Letters, 637 (1961).
109. M.I. Farberov, A.V. Bondarenko, V.M. Obukhov, and G.I. Karakhuleva, Dokl. Akad. Nauk SSSR, 179, 1359 (1968).
110. G.I. Karakuleva, A.V. Bondarenko, M.I. Farberov, and Z.V. Smirnova, Neftekhimiya, 5, 856 (1965).
111. A.V. Bondarenko, M.I. Farberov, G.I. Karakuleva, and G.N. Shustovskaya, Neftekhimiya, 8, 79 (1968).
112. M. Konovalov and I. Egorov, Zhur. Russ. Khim. Obshch., 30, 1031 (1898).
113. E.S. Pokrovskaya and T.G. Stepantseva, Zhur. Obshch. Khim., 9, 1953, 2291 (1939).
114. I.I. Lebedev, Uspekhi Khim., 21, 1399 (1952).
115. M. Inatome, J. Amer. Chem. Soc., 74, 192 (1952).
116. B.S. Friedman, F.L. Morritz, C.J. Morrissey, and R. Koncos, J. Amer. Chem. Soc., 80, 5867 (1958).
117. B.S. Friedman and F.L. Morritz, J. Amer. Chem. Soc., 78, 2000 (1956).
118. S.V. Lebedev and E.P. Filonenko, Zhur. Russ. Khim. Obshch., 57, 127 (1925).
119. V.V. Korshak, "Khimiya Vysokomolekulyarnykh Soedinenii" (The Chemistry of Macromolecular Compounds), Izd. Akad. Nauk SSSR, Moscow–Leningrad, 1950, p. 178.
120. V.V. Korshak and K.K. Samplavskaya, Dokl. Akad. Nauk SSSR, 59, 497 (1948).
121. A.M. Butlerov, Zhur. Russ. Fiz.-Khim. Obshch., 5, 187 (1873).
122. E.E. Vagner, Zhur. Russ. Khim. Obshch., 1230 (1880).
123. F. Whitmore, Chem. Eng. News, 26, 668 (1948).
124. T. Fabry, Chem. Listy, 59, 578 (1965).
125. N.S. Viswanathan and L. Keven, J. Amer. Chem. Soc., 89, 2482 (1967).
126. W.H. Saunders, Jnr., "Ionic Aliphatic Reactions" (Translated into Russian), Izd. Mir, 1967, p. 112.
127. Yu.G. Osokin, V.Sh. Fel'dblyum, and S.I. Kryukov, Zhur. Org. Khim., 6, 691 (1970).
128. Yu.U. Osokin, S.I. Kryukov, and V.Sh. Fel'dblyum, Zhur. Org. Khim., 6, 1542 (1970).
129. D. Cram, see Ref. 9, p. 314.
130. H.C. Brown and J. Moritani, J. Amer. Chem. Soc., 77, 3623 (1955).
131. E.D. Hughes, C.K. Ingold, and V.J. Shiner, J. Chem. Soc., 3827 (1953).
132. M.L. Dhar, E.D. Hughes, and C.K. Ingold, J. Chem. Soc., 2093 (1948).
133. V.V. Korshak and N.G. Matveeva, Dokl. Akad. Nauk SSSR, 78, 1145 (1951).
134. S.V. Lebedev, "Zhizn' i Trudy" (Life and Work), Khimteoretizdat, Leningrad, 1938.
135. P. Vaculik, "Chemie Monomeru" (Translated into Russian), Inostr. Lit., Moscow, 1960, p. 620.
136. Kh.S. Bagdasar'yan, "Teoriya Radikal'noi Polimerizatsii" (Theory of Radical Polymerisation), Izd. Nauka, Moscow, 1966.
137. S.V. Lebedev, "Issledovaniya v Oblasti Polimerizatsii Dvuetilenovykh Uglevodorodov" (Studies on the Polymerisation of Diene Hydrocarbons), St. Petersburg, 1913.
138. S.V. Lebedev, G.G. Koblyanskii, and A.I. Yakubchik, Zhur. Russ. Fiz. Khim. Obshch., 56, 265 (1927).
139. B.A. Kazanskii and G.T. Tetevosyan, Zhur. Obshch. Khim., 9, 1458 (1939).
140. B.A. Kazanskii, "Kataliticheskie Prevrashcheniya Uglevodorodov" (Catalytic Reactions of Hydrocarbons), Izd. Nauka, Moscow, 1968.
141. M.I. Rozengart and B.A. Kazanskii, Uspekhi Khim., 40, 1537 (1971) [Russ. Chem. Rev., No. 9 (1971)].
142. I.N. Nazarov, Zhur. Obshch. Khim., 7, 702 (1937).
143. D.T. Flood and G. Calingaert, J. Amer. Chem. Soc., 56, 1211 (1934).
144. A. Morton and F. Fallwell, J. Amer. Chem. Soc., 59, 2387 (1950).
145. A.S. Onishchenko, "Dienovyi Sintez" (The Diels-Alder Synthesis), Izd. Akad. Nauk SSSR, Moscow, 1963.
146. H.J. Backer and J. Strating, Rec. Trav. chim., 53, 525 (1924).
147. H.J. Backer and J. Strating, Rec. Trav. chim., 58, 643 (1939).
148. K. Alder, Annalen, 571, 157 (1951).
149. H.J. Backer and J. Strating, Rec. Trav. chim., 58, 1280 (1939).
150. A.E. Favorskii and I.I. Nazarov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1309 (1933).
151. V.A. Sidorov, Khim. Prom., No. 7, 1 (1963).
152. A.N. Vinogradov, V.V. Voronenkov, and V.A. Belyaev, Zhur. Prikl. Khim., 41, 1344 (1970).
153. M. Gomberg, Ber., 33, 3150 (1900).
154. A.E. Chichibabin, "Issledovaniya po Voprosu o Trekhatomnom Uglerode" (Studies on Triatomic Carbon), Izd. Moskov. Gos. Univ., 1912.
155. H. Lankamp, W.T. Nauta, and C. Mac-Lean, Tetrahedron Letters, 249 (1968).
156. W.B. Smith, J. Chem. Educ., 535 (1970).
157. W.B. Smith and T.J. Kmet, J. Phys. Chem., 70, 4084 (1966).
158. V.V. Voronenkov, Yu.A. Shapiro, and O.P. Yablonskii, Uch. Trudy Yaroslavsk. Tekhnol. Inst., 14, 12 (1972).
159. S. Samoilov and M. Dyatkina, Zhur. Fiz. Khim., 22, 1294 (1948).
160. P. Jacobson, Ber., 38, 196 (1905).

Yaroslavl Technological Institute,
Institute of Synthetic Rubber Monomers