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# SYNTHESES AND REACTIONS IN THE CYCLOBUTANE SERIES

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## INTRODUCTION

A characteristic feature of the four-membered carbon ring is its instability, which is shown by the fact that in various reactions it readily undergoes isomerisation accompanied by a change in the carbon skeleton. This complicates syntheses in the cyclobutane series, since the preparation of even the simplest derivatives often requires complicated, roundabout routes in order to maintain the four-membered ring. Isomerisation of such a ring can involve not only enlargement and cleavage but also contraction to a three-membered ring.

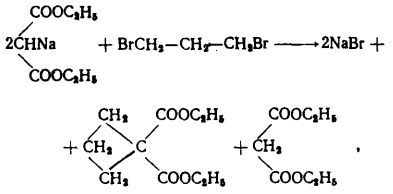
Isomeric changes in cyclobutane compounds have long attracted attention, and much work has been done on them. This field appears especially interesting in the light of recent work on the mechanism of isomerisation reactions. Such changes have been widely studied in cyclobutane compounds containing various functional groups, but very little work has been done on the hydrocarbons. This latter class of compounds has been altogether inadequately studied, probably owing to the difficulty of preparing cyclobutane hydrocarbons.

Several reviews have recently been published[1-5] on the synthesis and properties of various cyclobutane compounds, in which the hydrocarbons themselves do not receive much attention. Because of the abundance of miscellaneous information, it is not easy to obtain from these reviews an idea of the properties of the hydrocarbons, the difficulties in their preparation, or the advances which have recently been made in this direction. In the present review an attempt has been made to discuss in greater detail the chemistry of the cyclobutane hydrocarbons, and their synthesis, properties, and reactions. In order to give a more complete idea of the instability of the four-membered ring, the last section of the review will include an account of isomeric changes in cyclobutane derivatives covering the most recent work on this problem.

## I. SYNTHESIS OF HYDROCARBONS OF THE CYCLOBUTANE SERIES

Hitherto most hydrocarbons of the cyclobutane series have been obtained from diethyl cyclobutane-1,1-dicarboxylate and its homologues, *via* the monocarboxylic acids, the alcohols, aldehydes, and ketones. The most difficult stage on the way to the hydrocarbons, usually involving low yields, is the first stage, the preparation of the initial ester.

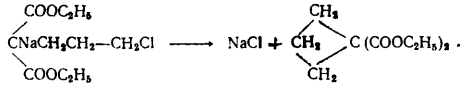
Diethyl cyclobutane-1,1-dicarboxylate was first obtained by Perkin[6] in 1887, by means of the reaction:



the yield of the ester being only 25%.

Many attempts have been described in the foreign literature to improve the yield in the Perkin's reaction, but they were unsuccessful, and the yield of the ester remained very low[7-11]. The authors of these papers were probably unacquainted with the published work of Russian scientists, who had succeeded in considerably improving the yields of the ester.

Thus Kizhner[12] modified Perkin's method as early as 1905, by replacing the 1,3-dibromopropane with 1-bromo--3-chloropropane. The different rates of reaction of the bromine and chlorine atoms in the latter compound with the sodium atom of the sodiomalonic ester result in the initial formation of 3-chloropropylmalonic ester, which then undergoes cyclisation:



By this method Kizhner obtained a 40% yield of diethyl cyclobutane-1,1-dicarboxylate.

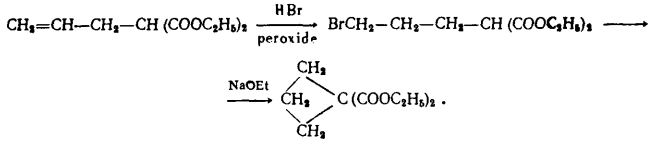
In 1941 Gol'mov and Kazanskii[13] undertook Kizhner's synthesis in two stages, and isolated the intermediate products. They found that, in the presence of sodium ethoxide, 3-chloropropylmalonic ester is readily converted (in 75–77% yield) into diethyl cyclobutanedicarboxylate. Consequently, the low yield in Kizhner's reaction is due, not to the difficulty of closing the four-membered ring, but to the great quantity of by-products obtained in the first stage of the reaction. Gol'mov and Kazanskii tried to find conditions which would increase the yield of the 3-chloropropylmalonic ester, and found that the use of 3 moles of malonic ester per mole of the bromochloropropane increases the yield of 3-chloropropylmalonic ester to 78.4% (compared with 52%). Thus carrying out the experiments in two stages raises the overall yield of diethyl cyclobutanedicarboxylate (based on the bromochloropropane) to 60%, which represents an increase by a factor of $1\frac{1}{2}$ compared with the yield in Kizhner's synthesis, and by a factor of $2\frac{1}{2}$ compared with Perkin's method.

Subsequently Gol'mov[14] studied the reaction of malonic ester with 1,3-dibromopropane, and found that varying the proportions of the reactants gave a considerable increase in yield. Thus he obtained a 70% yield of the ester by taking 4 moles of 1,3-dibromopropane and 4 moles of malonic ester per gramme-atom of sodium.

The last two methods, which show great improvements in the yield, have their disadvantages, since carrying out the reaction in two stages considerably lengthens the time required for the synthesis.

In 1949 Cason and Allen[15] described the preparation of cyclobutanedicarboxylic ester in 60% yield from malonic ester and 1,3-dibromopropane in one stage. In the opinion of Mariella and Raube[16], the ester obtained by this method contains about 14% of impurities, so they proposed a different method for its preparation, which gave a yield of about 55% of the unpurified ester or 43% of the pure ester[17]. This method hardly differs at all from that described by Kizhner.

An interesting process for obtaining the ester was suggested in 1949 by Walborsky[18]:



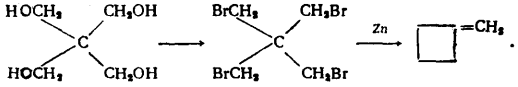
Diethyl allylmalonate was prepared in 80% yield by Linstead and Rydon's method[19], the overall yield of cyclobutanedicarboxylic ester being about 50% based on the diethyl allylmalonate.

Campbell and Rydon[20] suggested condensing the more reactive 1,3-diiodopropane with sodiomalonic ester, but the former substance must be synthesised specially, which considerably complicates the general method.

In conclusion we must consider the two-stage synthesis of diethyl cyclobutanedicarboxylate suggested in 1952 by Favorskaya and Yakovlev[21], the first stage of which takes place in absolute ether. The overall yield of the cyclic ester is here 80%, which far exceeds all the yields reported hitherto. The present reviewer, however, has been unable to reproduce this yield, and in many experiments carried out by this method the yield did not exceed 30%.

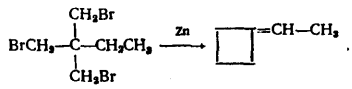
All the procedures reported above apply to reactions of malonic ester with dihalides in which both halogen atoms are attached to primary carbon atoms. The work of Ipat'ev[22] and of Kazanskii and Lukina[23] has shown that the course of the reaction is different when dibromides of different structure are used. The homologues of diethyl cyclobutanedicarboxylate can be used to prepare the corresponding disubstituted homologues of cyclobutane[24,25].

A great many investigations deal with another method of synthesising cyclobutane hydrocarbons, by the action of zinc dust on pentaerythritol tetrabromide[26]. This reaction, discovered by Gustavson[27], represents one of the simplest methods for obtained methylenecyclobutane from a readily available starting material:



The tetrabromide is usually obtained by the prolonged heating of pentaerythritol with a large excess of phosphorus tribromide[28]. Recently a new method has been suggested which considerably simplifies this synthesis[29].

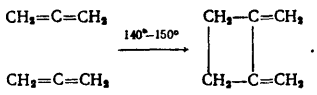
In a similar manner 1,1,1-trisbromomethylalkanes give good yields of alkenyl- and alkylidene-cyclobutanes[30,31]:



In all these syntheses, unfortunately, preparation of the initial polyhalogeno-compounds is associated with considerable difficulty.

In connection with this method of obtaining hydrocarbons, we must mention the work of Roberts and Sauer[32], who suggested many methods of converting methylenecyclobutane into cyclobutanol, cyclobutanone, and cyclobutane.

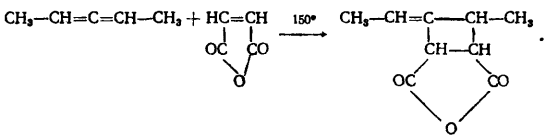
An interesting direction, in which new routes for the synthesis of cyclobutane hydrocarbons may be found, involves development of the dimerisation of allenes, discovered by Lebedev in 1911:[33,34]



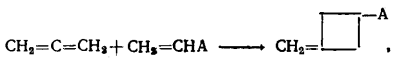
The low yields of the dimer reported by Lebedev and the difficulty of isolating it prevented this reaction from becoming in due course a preparative method for the synthesis of cyclobutane hydrocarbons.

In 1956 Blomquist and Verdol[35] succeeded in improving the method of dimerisation: they obtained an approximately 50% yield of the dimer, 1,2-dimethylenecyclobutane, by passing allene over glass beads heated to 500°–510°. The allene was prepared by the action of zinc dust on 2,3-dibromoprop-1-ene.

Another way of using allene was no less promising, consisting in its addition across a carbon–carbon double bond with the formation of cyclobutane and cyclobutene derivatives. In 1957 Alder and Ackermann[36] reported the addition of allenes to maleic anhydride. In the case of 1,3-dimethylallene a 60% yield of the adduct was obtained:

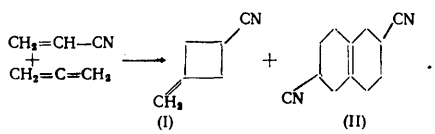


Shortly after this, Cripps *et al.*[37] published the first of a series of papers on the synthesis of substituted alkylidenecyclobutanes by the addition of allene to unsaturated compounds. They used this method to prepare methylenecyclobutanes containing a cyano, carboxy, alkoxycarbonyl, or aryl group in position 3:[38]



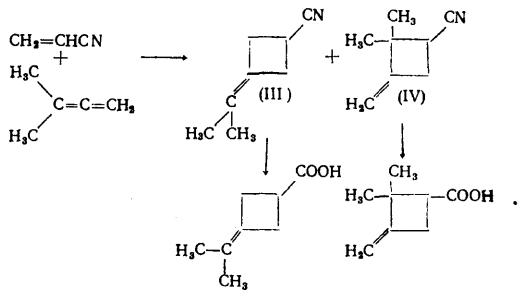
where A = CN, COOR, COOH, CHO, Ar.

Allene adds on especially smoothly to acrylonitrile, to give a cyclobutane derivative (I) and an octahydronaphthalene derivative (II):



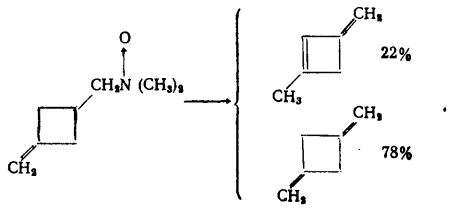
The reaction is carried out at 150°–250°, the maximum pressure during the reaction being about 4–4.5 atm. When a large excess of acrylonitrile is used, a 60% yield of I is obtained and a 15–20% yield of II. Under the conditions of the reaction the allene can undergo dimerisation to 1,2-dimethylenecyclobutane. The use of unsymmetrically substituted allenes in this reaction has shown that both double bonds can take part in addition with ring formation (cycloaddition).

Thus 1,1-dimethylallene reacts with acrylonitrile to give a 36% yield of 3-isopropylidenecyclobutyl cyanide (III) and 2,2-dimethyl-3-methylenecyclobutyl cyanide (IV). Alkaline hydrolysis of these compounds gives the corresponding acids, from which the hydrocarbons can be obtained:

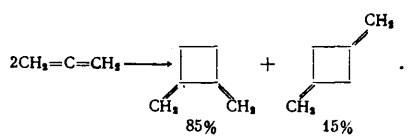


By using this method to obtain 3-methylenecyclobutyl cyanide, Caserio *et al.*[39] synthesised a series of 3-substituted methylenecyclobutanes.

At almost the same time, Williams and Sharkey[40] published the preparation of these same hydrocarbons by the pyrolysis of *NN*-dimethyl-3-methylenecyclobutylmethylamine oxide:



In the course of this work the interesting phenomenon was observed that heating the resulting mixture of hydrocarbons with a 10% solution of caustic potash in ethylene glycol produced a marked change in the relative proportions of the hydrocarbons. The product which was isolated consisted of 96% of 1-methyl-3-methylenecyclobutene and 4% of 1,3-dimethylenecyclobutane. Experiments which were then carried out on the dimerisation of allene showed that at 400° and atmospheric pressure the product is not pure 1,2-dimethylenecyclobutane, as would follow from the work of Lebedev[33] and of Blomquist and Verdol[35], but a mixture of 85% of this compound with 15% of the 1,3-isomer:

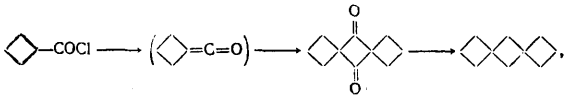


The process developed in this way permitted the preparation also of 3-isopropylidene-1-methylcyclobutene and 1,4,4-trimethyl-3-methylenecyclobutene.

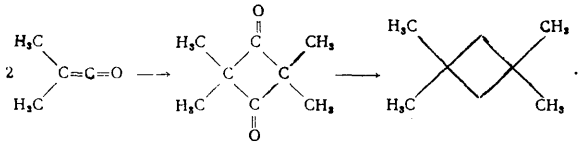
Migration of the double bond from the exocyclic position into the ring was observed also by Cripps *et al.*[41] in the action of excess of alkali on 3-methylenecyclobutane-1,2--dicarboxylic anhydride followed by acidification.

The above syntheses permitted for the first time familiarity to be gained with cyclobutane hydrocarbons containing double bonds in the side-chain or in the ring. It is easy to pass from these hydrocarbons to disubstituted saturated hydrocarbons.

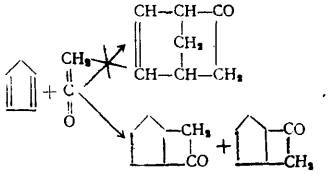
Another type of synthesis of hydrocarbons, which has been developed recently, appears to be of great interest. As early as 1912 Staudinger[42] found that ketoketens are able on standing to dimerise with the formation of substituted cyclobutane-1,3-diones. Buchman *et al.*[43] used this reaction to obtain a spiro-hydrocarbon according to the scheme:



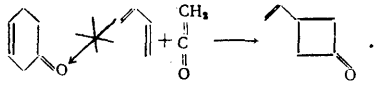
and also for the preparation of tetramethylcyclobutane[44]:



Staudinger also established that ketens are able to add on to a carbon–carbon double bond with the formation of cyclobutanones. Compounds containing conjugated double bonds can also undergo this reaction, diphenylketen being especially active in such reactions[45,46]. It was found that the addition of ketens to conjugated dienes never proceeds according to a diene synthesis mechanism:



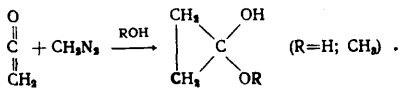
Vogel and Müller[47] have reported that keten reacts with butadiene to give a 66% yield of the 1,2-addition product, 3-vinylcyclobutanone:



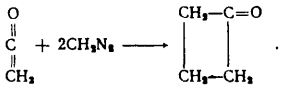
Reduction of the ketone by Kizhner's method gives vinylcyclobutane, from which ethylcyclobutane can be readily obtained. Application of this reaction to various dienes may provide wide opportunities for synthesising cyclobutane hydrocarbons of various structures.

Syntheses of cyclobutanone and its homologues (from which the hydrocarbons can be readily obtained) by the action of diazomethane on ketens are of great practical and theoretical interest. This reaction was discovered by Lipp and Köster[48] as long ago as 1931, but only recently have investigators paid more serious attention to it.

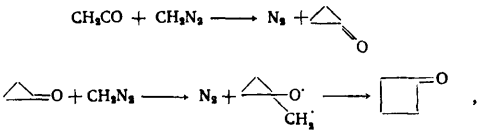
If keten is slowly run into an ethereal solution of diazomethane containing small amounts of methanol or of water, the hemiacetal or the hydrate of cyclopropanone is obtained in theoretical yield:



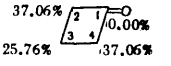
In the absence of water or alcohol, and with concentrated solutions of diazomethane at -70°, cyclobutanone is formed in 75% yield:



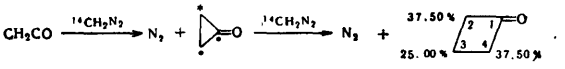
Lipp and Köster at first regarded this reaction as involving the intermediate formation of cyclopropanone:



but they later rejected this mechanism, since they considered it improbable that cyclopropanone would react smoothly with diazomethane in ether at -70°, while cyclobutanone would be stable under these conditions. In order to test the mechanism of this reaction, Semenow *et al.*[49] studied the reaction of keten with labelled diazomethane. The distribution of $^{14}C$ in the resulting cyclobutanone was

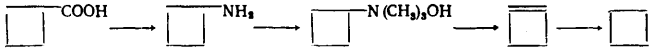


These results agree well with the hypothesis of the intermediate formation of cyclopropanone, from which cyclobutanone can be obtained equally probably by introducing a methylene group on either side of the carbonyl group:



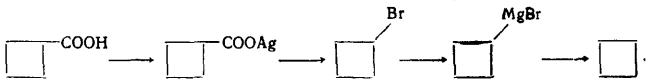
This equation gives the distribution of $^{14}C$ activity predicted for the intermediate formation of cyclopropanone. The high reactivity of this compound towards diazomethane may be associated, in the opinion of these workers, with the greater angular stress in a three-membered compared with a four-membered ring.

Kaarsemaker[50], using Lipp and Köster's method, obtained a 65% yield of cyclobutane by the Wolff–Kizhner reduction of cyclobutanone semicarbazone. Thus the overall yield of cyclobutane based on the diazomethane was 48%, which exceeded all yields of cyclobutane then available. Willstätter's method[51]

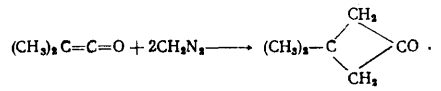


gives a 25% yield of cyclobutane based on cyclobutanemonocarboxylic acid, while the process more recently suggested

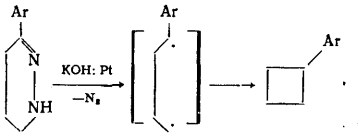
by Cason and Way gives a yield of about 40% based on the acid[52,53]:



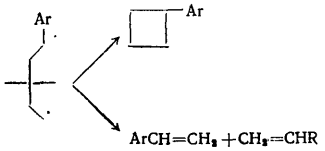
The reaction of substituted ketens with diazomethane may result in homologues of cyclobutane having the most varied structure. Thus Owen *et al.*[54] condensed diazomethane with dimethylketen and obtained 3,3-dimethylcyclobutanone:



A new method for the synthesis of arylcyclobutanes has been suggested by Levina *et al.*[55], who established that tetrahydropyridazines, the six-membered analogues of pyrazolines, on being heated in the presence of caustic potash and platinum to 250°–300°, decompose with the evolution of nitrogen and the formation of cyclobutane hydrocarbons:

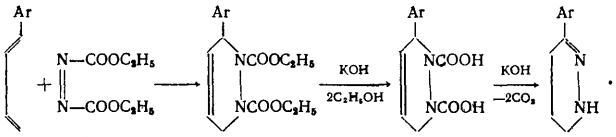


The intermediate diradicals undergo not only cyclisation to cyclobutane hydrocarbons but also cleavage with the formation of ethylenic hydrocarbons:

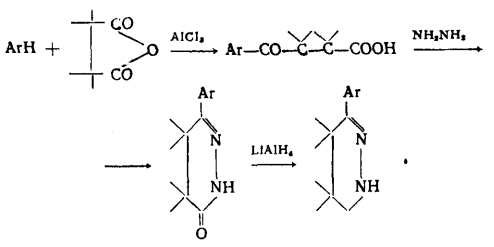


Sometimes the production of unsaturated hydrocarbons is the main reaction, and that of cyclobutane hydrocarbons a side-reaction. In the case of cyclobutylbenzene, its yield is 35%, while that of the styrene formed at the same time is 43%.

The applicability of the method was at first greatly restricted by the comparative difficulty of obtaining the starting materials for the synthesis, the tetrahydropyridazines. They were produced by hydrolysis accompanied by decarboxylation of adducts of diene hydrocarbons with diethyl azocarboxylate:



Recently Shabarov and his coworkers[56] have proposed a simpler method for synthesising 3-aryl-1,4,5,6-tetrahydropyridazines, from succinic anhydride:



By decomposing the corresponding tetrahydropyridazines they accomplished the first synthesis of *o*-, *m*-, and *p*-tolylcyclobutanes (in yields of 33.5, 20.5, and 32% respectively)[57], *o*- and *p*-methoxyphenylcyclobutanes (14.2 and 13.0%)[58], and also *p*-biphenylylcyclobutane (yield 41%)[58]. Unfortunately, this method cannot be used to obtain alkylcyclobutanes[59].

This brief survey of methods for synthesising hydrocarbons of the cyclobutane series shows that some progress has recently been made in this field. Comparatively simple routes for the synthesis of various hydrocarbons have already been developed. The chief difficulty is that at the present time the starting materials for these syntheses require special preparation, in several cases by a quite complicated path.

## II. PROPERTIES OF HYDROCARBONS OF THE CYCLOBUTANE SERIES

I have given some information on the electronic structure of cyclobutane in a review of work on the structure of cyclopropane[60]. According to modern views, the four-membered carbon ring, like the three-membered ring, involves distortion of the valency angles with the accompanying change in bond hybridisation, which is, however, considerably less strongly marked in this case than in cyclopropane[61,62].

For a long time it was assumed that, like the three-membered ring, a four-membered ring is planar. In 1952 Dunitz and Schomaker[63] made an electron diffraction examination of cyclobutane, and found that the four-membered ring is not planar but represents either a dihedron with an angle of about 160° (Fig. 1), or an insufficiently rigid planar ring with oscillations of large amplitude out of the plane. It was found that the H–C–H angles in cyclobutane are 114° ± 8°, the length of the C–H bonds is 1.09 ± 0.04 Å, and the length of the C–C bonds 1.56 ± 0.02 Å, which exceeds that of the C–C bonds in cyclopropane and the mean carbon–carbon bond length in general.

A little later the non-planar structure of cyclobutane was confirmed by comparing entropy values obtained from experimental data (heat capacities and heats of transition) with those calculated for a planar model, and also by the infrared spectra and by the calculated energies of formation and of isomerisation[64].

Recently Bastiansen and his coworkers repeated the electron diffraction examination of cyclobutane and cyclopentane, and have published preliminary results[65]. Values obtained for internuclear distances in cyclobutane were C–C 1.548 ± 0.003 Å and C–H 1.092 ± 0.010 Å. Thus the C–C bond is shown to be longer in saturated four-membered rings than in open-chain alkanes (1.536 Å for ethane and 1.533 Å for butane), but substantially shorter than found by Dunitz and Schomaker[63]. The paper mentions that the




Fig. 1.

cyclic carbon skeleton of cyclobutane and that of cyclopentane are non-planar, but the deviations from planarity were not determined with sufficient accuracy in the preliminary stage of the investigation.

From Seubold's data the mean energy of dissociation of the C–C bonds in cyclobutane is estimated[66] to be $60 \pm 3$ kcal mole$^{-1}$.

Carter and Templeton[67] found that at 173°K cyclobutane has a body-centred cubic lattice with a unit cell containing two molecules, the lattice constant being $a = 6.06 \pm 0.03$ Å.

Several of the constants of pure cyclobutane have been determined accurately — vapour pressure[68], boiling point (285.7°K)[69], and melting point (182.43°K)[70].

Information on cyclobutadiene can be found in the recent review by Vol'pin[71], and therefore we shall not discuss it here.

Derfer *et al.*[72] studied the infrared spectra of several alkylcyclobutanes, and at the same time those of many cyclopropane hydrocarbons. Comparison of the spectra opened up the possibility of determining hydrocarbons of both types in mixtures.

Roberts and his coworkers[39] studied the infrared and ultraviolet spectra of 1,3-dimethylenecyclobutane and related compounds. Loeffler *et al.*[73] investigated the absorption spectra in the far ultraviolet of cyclobutene, 1-methylcyclobutene, and methylenecyclobutane. Lord and Rea[74] examined the infrared absorption spectra of liquid and gaseous cyclobutene and hexadeuterocyclobutene, as well as their Raman spectra.

In 1956 Wren[75] studied the ultraviolet spectra of several cyclobutane compounds of the types:




and compared them with those of derivatives of the type ▷–X=Y, in which, owing to the unsaturated character of the three-membered ring, the absorption bands are displaced to longer wavelengths (bathochromic effect) and the intensities of the characteristic frequencies are increased (hyperchromic effect). Wren did not observe these effects in five cyclobutane compounds, which were found to show an auxochromic effect, *i.e.* a diminution in intensity of the characteristic frequencies, which he attributed to the influence of the four-membered ring.

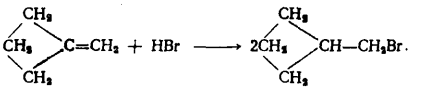
Aleksanyan and Sterin[76,77] examined the Raman spectra of sixteen alkylcyclobutanes and two unsaturated hydrocarbons of this series. The spectrum of isopropenylcyclobutane, a hydrocarbon having a double bond adjacent to the ring, showed no enhanced intensity of the characteristic frequencies such as was observed in the cases of isopropenyl- and vinyl-cyclopropanes. In other words, it would appear from the Raman spectra of isopropenylcyclobutane that there is no conjugation between the double bond and the four-membered ring, as in the cases reported by Wren.

Treshchova *et al.*[78] found that the intensities of the lines characteristic of the four-membered ring and of the benzene ring in the Raman spectra of several arylcyclobutanes are higher than in those of alkylbenzenes and alkylcyclobutanes. Hence it was concluded that conjugation exists between the two types of ring, although it is less strongly developed than in arylcyclopropanes.

As a result of advances in the synthesis of unsaturated hydrocarbons of the cyclobutane series, several papers have appeared on the behaviour of such hydrocarbons in various reactions. These investigations are comparatively rare, and are concerned mainly with the reactivity of the double bonds, not of the four-membered ring itself.

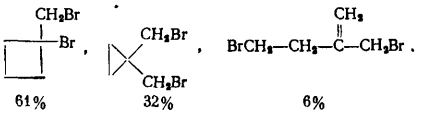
Thus Buchman and Howton[79] studied the Ziegler bromination of methylenecyclobutane, and found that reaction between *N*-bromosuccinimide and methylenecyclobutane in benzene in the presence of peroxides yielded a mixture of 14% of 2-bromomethylenecyclobutane and 56% of α-bromomethylcyclobutene. Cyclobutene under the same conditions gave 48% of 1,2-dibromocyclobutane and only 1% of 3-bromocyclobutene[80].

Krug *et al.*[81] reported the preparation of a 59% yield of bromomethylcyclobutane in the presence of a peroxide:

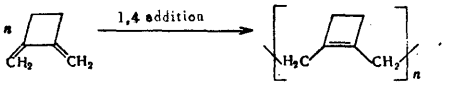



As was to be expected, this addition takes place contrary to Markovnikov's rule, and results in neither cleavage nor expansion of the ring.

Applequist and Roberts[82] obtained a mixture of dibromides by the reaction of methylenecyclobutane with bromine in carbon tetrachloride:




The properties of 1,2-dimethylenecyclobutane, studied by Blomquist and Verdol[83], proved to be of considerable interest. This hydrocarbon possesses two exocyclic double bonds conjugated through the cyclobutane ring, and very readily undergoes polymerisation. In this respect it resembles the previously investigated exocyclic dienes of the cyclohexane series[84]:

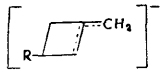



Emulsion polymerisation of dimethylenecyclobutane at 50° for 24 h gave a 100% yield of polymer. Analysis showed that the latter contained about 80% of the 1,4-addition product and 20% of the 1,2 product. The great readiness of 1,2-dimethylenecyclobutane to undergo polymerisation was confirmed by comparing its behaviour with that of 2,3-dimethylbuta-1,3-diene under these conditions. Dimethylenecyclobutane gave a 96% yield of polymer, while the open-chain diene gave only 13% under the same conditions. Furthermore, 1,2-dimethylenecyclobutane was very active in the Diels–Alder reaction, giving adducts with maleic anhydride and with *N*-phenylmaleimide.

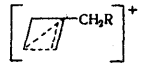
Applequist and Roberts[82] investigated the polymerisation of the compounds methylenecyclobutene (V), 3,3-dimethyl-4-methylenecyclobutene (VI), and 3′-methylenecyclobut-1′-enylbenzene (VII), which they had synthesised. Anionic polymerisation of all three hydrocarbons in the presence of sodamide and potassamide in liquid ammonia or of sodamide in benzene gives polymers of relatively low molecular weight. Radical polymerisation of V and VII takes place readily on standing in air, giving polymers of higher

molecular weight than in the first case. The compound VI shows less tendency to radical polymerisation. Cationic polymerisation of V under the influence of boron trifluoride goes extremely rapidly with formation of a polymer having the highest molecular weight.

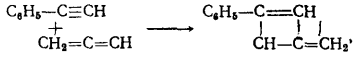
These investigators consider that anionic polymerisation involves the intermediate formation of an anion of the type



and cationic polymerisation that of a cation of the type



having a 1,3 $\pi$-bond. The possible existence of such a cation is supported by LCAO calculations. In this work 3′-methylenecyclobut-1′-enylbenzene was obtained in 1% yield by the reaction:



and 3,3-dimethyl-4-methylenecyclobutene from pinene *via* pinic acid.

Recently Shabarov *et al.*[85] have studied the behaviour of cyclobutylbenzene in several reactions, and have shown that, even under comparatively severe conditions, the four-membered ring of this hydrocarbon is stable in the presence of mercuric acetate (which readily cleaves a three-membered ring), and it also does not undergo alkylation in the presence of aluminium chloride.

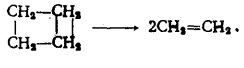
Nitration and acylation of cyclobutylbenzene resulted in substitution in the benzene ring, while the four-membered ring remained unchanged.

## III. REACTIONS OF HYDROCARBONS OF THE CYCLOBUTANE SERIES

Cyclobutane and its homologues, like the alkanes, are inert towards most chemical reagents. The comparatively few papers which have been published on their reactivity are concerned mainly with thermal and catalytic reactions — decomposition, isomerisation, and hydrogenolysis.

### (*a*) Thermal Decomposition and the Isomerisation of Hydrocarbons

Genaux *et al.*[86] in 1953 studied the thermal decomposition of cyclobutane, and found that at 420°–480° ethylene is formed:



Later Langrish and Pritchard[87] studied the kinetics of the thermal decomposition of equimolecular mixtures of $C_4H_8 + C_4D_8$ at 431°–485° and 0.7–36 mm Hg. Analyses were made with a mass spectrometer. No compounds of the type $C_2H_2D_2$ were detected among the decomposition products (ethylenes), which indicates that free radicals are not formed in the course of thermal decomposition. According to these workers, the latter is a purely unimolecular reaction. A similar conclusion concerning reaction order was reached by Srinivasan and Kellner[88] from a study of the thermal decomposition of 1,1,2,2-tetradeuterocyclobutane.

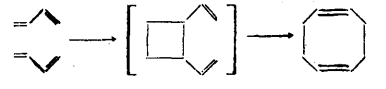
Cooper and Walters[89] showed that the four-membered ring is considerably less stable in cyclobutene than in cyclobutane. Thus they obtained buta-1,3-diene from cyclobutene at temperatures as low as 130°–175°. The reaction velocity was independent of the ratio of surface to volume of the reaction vessel and was unaffected by replacement of Pyrex glass by quartz, which indicates that the reaction is homogeneous in character. From the fact that additions of nitric oxide and propene have no inhibiting effect it was concluded that this reaction does not involve free radicals.

Subsequently Walters and his coworkers investigated the thermal decomposition of ethylcyclobutane[90], methylcyclobutane[91], propylcyclobutane[92], and *cis*-1,2-dimethylcyclobutane[93], and found that the rate of decomposition is increased by the introduction of methyl groups into cyclobutane. Thus at 430° methylcyclobutane decomposes more rapidly than cyclobutane by a factor of 1.5, and dimethylcyclobutane by a factor of 4.

The thermal decomposition of methylenecyclobutanes was studied by Drysdale *et al.*[94], who suggested that, since the weakest site in such compounds is the allyl bond, thermal cleavage may lead to the intermediate formation of one or two diradicals.

It can be concluded from the above work that the presence of a double bond in either the four-membered ring or a side-chain considerably diminishes the stability of the ring towards heat.

The thermal isomerisation of *cis*-1,2-divinylcyclobutane, accompanied by enlargement of the ring, was observed by Vogel[95] in an investigation of the mechanism of the formation of cycloocta-*cis*-1,*cis*-5-diene. He suggested that formation of this hydrocarbon by thermal dimerisation of butadiene in absence of a catalyst takes place by 1,2–1,2 addition with intermediate formation of *cis*-1,2-divinylcyclobutane:



Vogel assumed that, as a result of the interaction of the adjacent vinyl groups, divinylcyclobutane would be unstable, and pass into cycloocta-1,5-diene under the conditions of the reaction. In order to test this hypothesis, *cis*-1,2-divinylcyclobutane was synthesised, and was actually found to isomerise into cycloocta-*cis*-1,*cis*-5-diene at as low a temperature as 120°.

Little has been published on the catalytic isomerisation of hydrocarbons of the cyclobutane series. Ipat'ev and Tikhotskii[96] studied the isomerisation of methylenecyclobutane in the presence of alumina at 290°–300° and found that under these conditions the ring opened to form a diene, whose structure was not established.

Quite different results were obtained by Filipov[97] in experiments on methylenecyclobutane in the presence of aluminium oxide at 300°. According to his observations, almost complete isomerisation to methylcyclobutene took

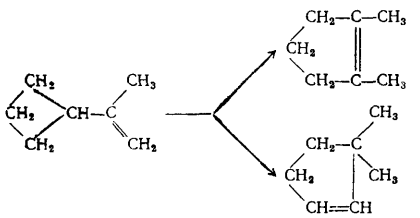
place. Doyarenko[98] studied the isomerisation of methylenecyclobutane over aluminium oxide at higher temperatures (400°–430°). Several reactions took place at the same time — isomerisation to isoprene, hydrogenation, dehydrogenation, and polymerisation. As a result, the reaction products were found to contain cymene, a rubberlike polymer, 2-methylbut-2-ene, propene, and gaseous products.

In 1929 Rozanov[99] investigated the isomerisation of methylcyclobutane in the presence of aluminium oxide and thorium oxide. The reaction products, identified solely by their boiling points, were pent-2-ene and 2- and 3-methylbut-1-enes.

The behaviour of hydrocarbons of the cyclobutane series under conditions favouring isomerisation was subsequently studied by Kazanskii, Lukina, and their coworkers[100,101]. All experiments were carried out in such a way that the stabilities of the four-membered and three-membered rings could be compared. It was found that, in the presence of all the catalysts producing isomerisation of the three-membered ring under comparatively mild conditions, the ring in alkylcyclobutanes was stable even at considerably higher reaction temperatures[100]. Even at 250° aluminium silicate produced no change in the constants of ethyl- and isopropyl-cyclobutanes, and kieselguhr caused no variation either at 150°, 300°, or 400°. It was only at 500° that the resulting product differed markedly in constants from the initial hydrocarbon, but such change can be attributed to the high temperature.

Under conditions of chromatographic adsorption analysis, even without additional cooling, the ring in alkylcyclobutanes, in contrast to that in alkylcyclopropanes, underwent no change. As a result, this method has been employed successfully for the purification of such hydrocarbons from contaminants[101].

The same workers found that cyclobutane hydrocarbons containing a double bond in a side-chain behave quite differently under isomerisation conditions[100]. Thus isopropenylcyclobutane on contact with silica gel at room temperature was completely isomerised with expansion to a five-membered ring:



These results agree well with the behaviour of pinene, which according to Arbuzov and Isaeva[102] isomerised to a mixture of bornane, *p*-mentha-1,8-diene, and *p*-mentha-1,4(8)-diene when an attempt was made to purify it by chromatographic adsorption on silica gel.

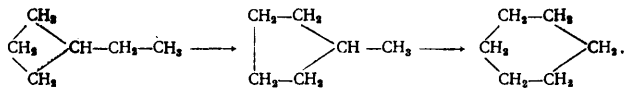
Subsequently Lukina, Kazanskii, and their collaborators showed[100] that, in the presence of kieselguhr at 200°, isopropenyl- and isopropylidene-cyclobutane are completely isomerised with the formation of the same mixture of unsaturated hydrocarbons of the cyclopentane series. The hydrogenated product of the isomerisation was a mixture of 1,2- and 1,1-dimethylcyclopentanes.

Both the catalysts investigated are able to cause migration of the double bond, and it can therefore be supposed that in both cases (isopropenyl- and isopropylidene-cyclobutane) the same unsaturated hydrocarbon had reacted.

It has thus been shown that the four-membered ring is considerably more stable than the three-membered ring under conditions of catalytic isomerisation. Only cyclobutane hydrocarbons containing a double bond in the substituent form an exception. In the presence of acidic catalysts, *i.e.* under conditions favourable to the formation of a carbonium ion, such hydrocarbons isomerise as readily as do alkylcyclopropanes.

Interesting results have been obtained from a study of the isomerisation of alkylcyclobutanes in the presence of more active catalysts. Turova-Polyak and Lukina[103] examined the isomerisation of ethylcyclobutane in the presence of aluminium chloride, the reaction conditions being chosen to permit comparison with the behaviour in this reaction of cyclopentane hydrocarbons, which had been studied earlier by Turova-Polyak and her coworkers[104–112]. The relative proportions of ethylcyclobutane and aluminium chloride were 3 : 1, and it was intended to carry out the reaction by prolonged boiling, as with cyclopentanes. However, the reactivity of the cyclobutane hydrocarbon was quite different: a vigorous exothermic reaction took place on contact with the aluminium chloride even at room temperature. Among the reaction products were detected methylcyclopentane and cyclohexane to the extent of 36–37% of the total. Isomerisation was accompanied by alkylation of the cyclohexane and polymerisation of the decomposition products of ethylcyclobutane with the formation of saturated hydrocarbon fractions of high boiling point.

In the view of these workers, the isomerisation of ethylcyclobutane takes place in stages:



Such a reaction mechanism is confirmed by the presence of methylcyclopentane among the reaction products, and this readily isomerises into cyclohexane, the most stable system under the experimental conditions. Thus it has been shown in this work that a four-membered ring is considerably less resistant to reaction with aluminium chloride than are five- and six-membered rings.

A little later this type of isomerisation was studied by Ipatieff† and his coworkers[113] with methyl-, ethyl-, and isopropyl-cyclobutane as examples.

Ipatieff *et al.*[114] described the reaction of methylcyclobutane with benzene in the presence of sulphuric acid, and found that here, as in the case of olefins and cyclopropanes[115,116], the benzene ring underwent alkylation. This was preceded by isomerisation of the four-membered ring under the influence of the sulphuric acid. However, these latter results are open to doubt, since the initial hydrocarbon used in the experiment was impure, the t-pentylbenzene (1.5 ml) which resulted from the reaction boiling over a range of 15°.

Summarising the little work which has been done on the reactions of cyclobutane hydrocarbons, we can conclude that cyclobutane and its homologues are quite stable towards

† Ipat'ev (Ed. of Translation).

heat and catalysts. The four-membered ring is considerably less stable in unsaturated hydrocarbons. In most cases the action of heat leads to cleavage of the ring, while the action of catalysts results in ring enlargement.

### (*b*) Catalytic Hydrogenation of Hydrocarbons of the Cyclobutane Series

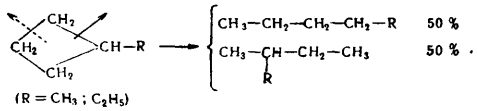
One of the most characteristic reactions of cyclobutane hydrocarbons is the catalytic addition of hydrogen with cleavage of the ring (hydrogenolysis). In 1907 Willstätter and Bruce [117] observed that, when cyclobutane is passed together with hydrogen over finely divided nickel at 180°, it is converted into n-butane. In 1911 Lebedev [118] showed that heating 1,2-diisopropylcyclobutane at 275° in hydrogen under a pressure of 100 atm results in opening of the four-membered ring. Later Rozanov [119] reported that, when methylcyclobutane is hydrogenated in the presence of freshly reduced nickel at 210°, isopentane is formed.

Raik [120,121] hydrogenated methyl-, ethyl-, and propyl-cyclobutane in the presence of platinised carbon, and found that fission of the C–C bonds of the four-membered ring starts at about 260°. In his view, the bond one carbon atom distant from that linked to the substituent undergoes rupture. As in all the previous work, quite primitive methods were used to analyse the reaction products in Raik's investigation. This casts doubt on his conclusions concerning the selective cleavage of the four-membered ring in this reaction.

The temperature limits of hydrogenolysis given by Raik are probably governed by the feeble activity of the catalyst, since the five-membered cyclopentane ring, which can be expected to be more stable, is already broken at 225° in the presence of platinised carbon [122].

Kazanskii, Lukina, and their collaborators [123-127] made a more detailed study of the hydrogenolysis of alkylcyclobutanes in the presence of platinised and palladised carbon. They established the temperature limits at which cleavage of the four-membered ring occurs with addition of hydrogen, and determined the way in which the ring breaks. They found that, in the presence of platinised carbon, hydrogenolysis begins at 150° and goes to completion at 250°. [123]

On palladised carbon a rather higher temperature (290°) is required for hydrogenolysis [127]. Cleavage of the four-membered ring on both catalysts takes place in all possible ways, with the formation of approximately equal quantities of isomeric alkanes:




In the case of isopropylcyclobutane, the bond farthest from the substituent was broken to a rather greater extent than the adjacent bond [125].

The hydrogenolysis of disubstituted homologues of cyclobutane — the 1,3-dimethyl and 1-ethyl-3-methyl derivatives — was also examined under comparable conditions [123]. They were found to undergo hydrogenolysis at approximately the same rate as the monosubstituted cyclobutane hydrocarbons.

The stabilities of the three-, four-, and five-membered rings to hydrogenolysis have been compared by hydrogenating ethylcyclopropane, methylcyclobutane, and cyclopentane in the presence of the same specimen of platinum catalyst [124].

The reactions of hydrocarbons of the cyclobutane series are of considerable interest because they provide an opportunity of assessing the stability of the four-membered ring in compounds containing no atoms other than carbon and hydrogen. Moreover, the investigations can be carried out with hydrocarbons which can be obtained comparatively easily in a high state of purity.

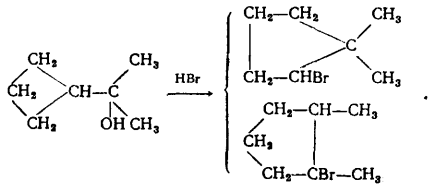
However, a study of the literature on a wider range of cyclobutane compounds shows that the information given here cannot completely characterise the stability of the four-membered ring and also give an idea of the changes in the carbon skeleton accompanying isomerisation. As already mentioned in the introduction, isomeric changes have been studied mainly with cyclobutane derivatives containing functional groups. The survey given below of work on this problem will enable a more correct idea to be obtained of the four-membered ring.

## IV. ISOMERIC CHANGES IN SOME DERIVATIVES OF CYCLOBUTANE

### (*a*) Isomerisation with Ring Enlargement

Among the early investigations in this field was Kizhner's work on isomeric changes in tertiary alcohols of the cyclobutane series. He first synthesised cyclobutyldimethylcarbinol as starting material for the preparation of cyclobutane hydrocarbons, but the properties of this compound at once attracted his attention, since under various conditions the alcohol is converted with exceptional ease into a cyclopentane derivative [128-130].

Thus heating cyclobutyldimethylcarbinol with excess of fuming hydrobromic acid gave a mixture of two bromocyclopentanes:




Gaseous hydrogen iodide already gave analogous derivatives at 0°, whereas at 200°–210° it produced more profound isomerisation, yielding 1,2-dimethylcyclopentane contaminated with a little methylcyclohexane.

The action on cyclobutyldimethylcarbinol of oxalic and dilute sulphuric acids [131], and also of acetic anhydride, produced isomerisation to 2,2-dimethylcyclopentanol. Similar isomerisation occurred with cyclobutyldiethylcarbinol [132]. It was only in the case of cyclobutyldiphenylcarbinol [133] that dehydration with oxalic acid was not accompanied by isomerisation, the product of the reaction being a cyclobutane hydrocarbon.

Chavanne and Chiurdoglu [134] used toluene-*p*-sulphonic and formic acids as dehydrating agents, and in both cases observed enlargement of the cyclobutyldimethylcarbinol ring to a five-membered ring.

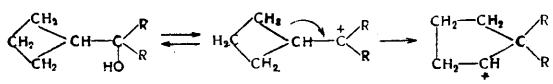
At a later date Favorskaya and Yakovlev published a series of papers[135-138] on the reaction of tertiary cyclobutane alcohols with dilute hydrochloric and sulphuric acids. They studied the behaviour in this reaction of cyclobutyldiisopropylcarbinol and of the corresponding ethyl-, methyl-, and isopropyl-phenyl derivatives. From a comparison of their results with those of Kizhner, they concluded that the tendency of the alcohol to isomerise is diminished on replacement of an alkyl by an aryl radical. Thus in the cases of cyclobutylethyl(and methyl)phenylcarbinols the four-membered ring was preserved on dehydration with hydrochloric and sulphuric acids.

With increase in size of the alkyl radical the direction of the reaction changed, and in the case of cyclobutylisopropylphenylcarbinol, as with cyclobutyldiisopropylcarbinol, isomerisation took place, with or without dehydration depending on the conditions of the reaction.

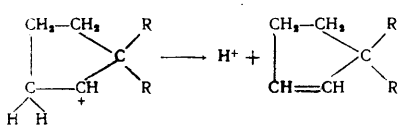
Not only tertiary but also primary and secondary alcohols of the cyclobutane series are characterised by a tendency to isomerise under the influence of acidic reagents. Dem'yanov[139] studied the changes undergone by cyclobutylcarbinol on treatment with oxalic and sulphuric acids, and Tatevosyan *et al.*[140] those undergone by the secondary alcohol, cyclobutylmethylcarbinol.

All these investigations show that acidic reagents are unsuitable for the conversion of cyclobutylcarbinols into the corresponding cyclobutane hydrocarbons, as in all these cases isomerisation with ring enlargement takes place to give cyclopentane derivatives.

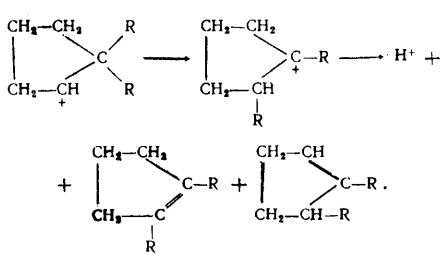
The changes undergone by cyclobutane alcohols under the influence of acidic reagents can be represented by the general formulae



Stabilisation can occur either by transfer of an electron pair to the electron-deficient carbon atom without migration of a proton:

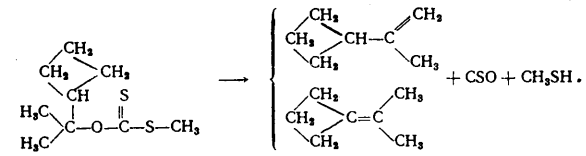


as a result of which a multiple bond is formed; or by capture of the electron pair together with the alkyl group from the adjacent carbon atom:



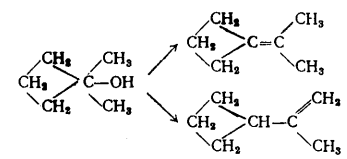
As early as 1936 Kazanskii[141] succeeded in dehydrating cyclobutyldimethylcarbinol without changing the carbon skeleton, by pyrolysis of the xanthate (Chugaev's method).

A low yield of a mixture of hydrocarbons was obtained as follows:



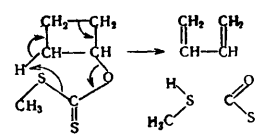
In 1953 Ipatieff and his coworkers[142] dehydrated the alcohol by heating it with phenyl isocyanate. A mixture of unsaturated hydrocarbons was obtained, hydrogenation of which gave isopropylcyclobutane. These workers assumed that the reaction involves the formation of phenylurethane, the mechanism of whose decomposition is similar to that suggested by Hückel *et al.*[143] for the Chugaev reaction.

Kazanskii *et al.*[144] obtained the corresponding unsaturated hydrocarbons of the cyclobutane series (in 75–90% yield) by boiling the alcohols with a few drops of concentrated sulphuric acid and simultaneously distilling off the products of dehydration:

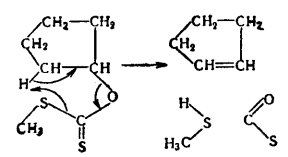


This method was used to dehydrate cyclobutyl-dimethyl-, -ethylmethyl-, and -diethyl-carbinols[145]. Under these conditions alcohols or hydrocarbons containing a five-membered ring are not formed at all.

Cyclobutanol behaves in a very interesting manner under conditions of dehydration. In an attempt to dehydrate it in the presence of aluminium oxide at 360°–390°, Doyarenko[146] obtained a mixture of propene and butadiene. Roberts and Sauer[32] tried to use the Chugaev method for the dehydration, but here, too, almost pure buta-1,3-diene was obtained:



On the other hand, when this method was applied to cyclopentanol, a 70% yield of cyclopentene was obtained:

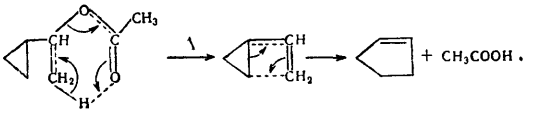


In the view of these workers[32], the cyclobutane ring undergoes fission during pyrolysis of the xanthates.

It is probable that pyrolysis does not always result in fission of the four-membered ring. Thus Overberger and Borchert[147] observed a new thermal rearrangement, accompanied not by fission but by enlargement of the ring, in the pyrolysis of acetates containing small rings. They showed that the main pyrolytic product of 1-cyclopropylethyl acetate was cyclopentene, and that 1-cyclobutylethyl acetate gave cyclohexene. It is interesting that in the case

of 1-cyclopentylethyl acetate enlargement of the ring was not observed, the normal reaction product, vinylcyclopentane, being obtained.

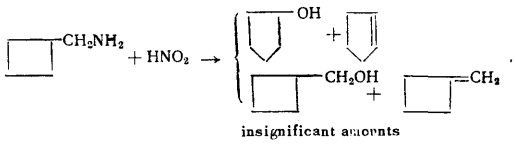
Pyrolysis was carried out at 500°–510°. It was assumed that, in the case of 1-cyclopropylethyl acetate, cyclopentene was formed mainly from vinylcyclopropane:



In order to test this hypothesis, vinylcyclopropane in acetic acid was subjected to pyrolysis under identical conditions, when 40% of it was converted into a mixture of 95% of cyclopentene and 5% of penta-1,4-diene. This rearrangement is especially interesting in that here the ring is enlarged by two carbon atoms instead of by only one.

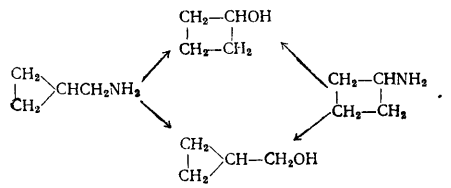
(*b*) Isomerisation Accompanied by Ring Enlargement, Contraction, and Cleavage

In 1903 Dem'yanov [148,149] found that the main product of the action of nitrous acid on cyclobutylmethylamine was a mixture of alcohols and hydrocarbons consisting predominantly of cyclopentane derivatives:

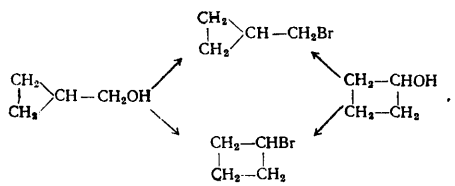


insignificant amounts

This remarkable discovery led Dem'yanov to make a broad study of the action of nitrous acid on cyclic amines [150]. In the course of this he disproved the results of Perkin [151] and of Dalle [152] on the synthesis of cyclobutanol and of cyclopropylcarbinol by the action of nitrous acid on the corresponding amines. He showed that in fact both cyclopropylmethylamine and cyclobutylamine yield a mixture of the above two alcohols on treatment with nitrous acid [153]:



Dem'yanov isolated both alcohols in the pure form, and made a thorough study of their properties. It was later found that a similar isomerisation of a three-membered into a four-membered ring, and conversely, takes place in other reactions as well. For example, cautious treatment of both alcohols with hydrobromic acid gives a mixture of cyclobutyl and cyclopropylmethyl bromides:



Dem'yanov concluded from this investigation that ring enlargement occurs when a $CH_2NH_2$ or $CH_2OH$ side-chain is present. When the amino- and hydroxy-groups are attached directly to a cyclic carbon atom, the ring size is always maintained.

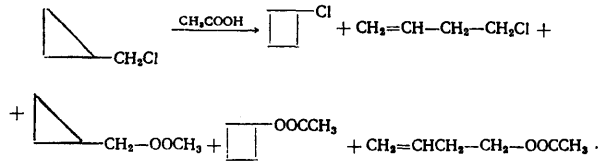
More recently, Smith and McKenzie extended these observations, and showed that treatment of cyclopropylcarbinol with phosphorus tribromide yields a bromide which reacts with magnesium and carbon dioxide to give pent-4--enoic acid [154]. According to the observations of Bruylants [155] and also of Favorskaya and Fridman [156], cyclopropyldimethylcarbinol reacts with hydrogen chloride to form 5-chloro-2-methylpent-2-ene, which passes back into the carbinol on hydrolysis.

A systematic study of this most interesting phenomenon was begun by Roberts and his coworkers in 1945, and has continued to the present time [157–165].

Studying the synthesis and properties of compounds having small rings, Roberts found that most reactions of cyclopropylmethyl‡ and of cyclobutyl derivatives having a carbonium ion type of mechanism yield the same mixtures of reaction products, independently of whether the starting material contains a three-membered or a four-membered ring. In his opinion this is due to the astonishing ease of intramolecular changes in cyclobutyl and cyclopropylmethyl derivatives which is observed in reactions of a certain type. Roberts and his collaborators observed such changes in the vapour-phase chlorination of methylcyclopropane, in reactions of cyclopropylcarbinol with thionyl chloride and Lucas's reagent, in the reactions of cyclopropylmethylamine, cyclobutylamine, and but-3-enylamine with nitrous acid [161,164], in the hydrolysis and acetolysis of cyclopropylmethyl and cyclobutyl chlorides, and in Grignard reactions with cyclopropylmethyl halides [157,158]. Among all the reactions investigated, it was only in the reaction of but-3-enol with thionyl chloride, the vapour-phase chlorination of cyclobutane in the light, and Grignard reactions of but-3--enyl and cyclobutyl halides that internal rearrangement was not observed.

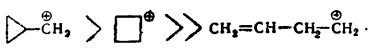
Roberts and Mazur's investigation [157,159] of the solvolysis of cyclopropylmethyl chloride was especially interesting. They prepared it by the photochemical chlorination of methylcyclopropane. Solvolysis of the chloride with acetic acid and several other solvents showed it to be extremely reactive. Thus the rate constant for the solvolysis of cyclopropylmethyl chloride in 50% aqueous ethanol exceeds the constant for cyclobutyl chloride by a factor of 27, and the constant for methylallyl chloride by a factor of 40 (allyl chloride itself did not react at all at this temperature).

These results were unexpected, since secondary halides usually undergo solvolytic reactions more readily than primary halides. It was also observed that solvolysis was accompanied by internal rearrangement of the cyclopropylmethyl chloride to form a 1.7 : 1 mixture of the less reactive cyclobutyl and but-3-enyl chlorides (on acetolysis). The products of acetolysis were cyclopropylmethyl and cyclobutyl acetates in the proportions 2.6 : 1, perhaps contaminated with small amounts of but-3-enyl acetate:



‡ The Russian reviewer felt it desirable to retain Roberts' "carbinyl" nomenclature, but in the translation this has been replaced by standard nomenclature (Ed. of Translation).

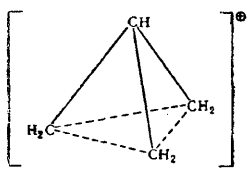
From the comparative solvolytic reactivity of cyclobutyl, cyclopropylmethyl, and but-3-enyl halides, the stability sequence of the corresponding carbonium ions is probably



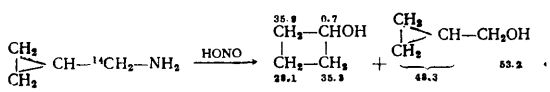
The composition of the products of carbonium-ion reactions accompanied by interconversions could have been expected on the assumption that classical cyclopropyl and cyclobutyl cations were formed as intermediates, between which equilibrium was established very rapidly. However, this hypothesis cannot explain the unusual tendency to solvolysis of both cyclopropylmethyl and cyclobutyl derivatives. Indeed, although the reactivity of compounds containing a three-membered ring can be explained by the diminution in stress in the transition state of solvolysis due to the direct formation of a cyclobutyl cation, this explanation cannot be applied to the reactivity of compounds containing a four-membered ring if they do not directly form but-3-enyl cations. This possibility is excluded by the fact that but-3-enyl derivatives have been observed only in small quantities as products of an irreversible reaction.

The ease of interconversion of cyclobutyl, cyclopropylmethyl, and but-3-enyl derivatives, together with the abnormal tendency of cyclopropylmethyl chloride to undergo solvolysis, to rearrange into isomeric chlorides, and to form rearranged solvolysis products, led these investigators to the view that such reactions involve the formation not of classical carbonium ions but of a common cationic intermediate compound[159,160].

Such an intermediate compound should embody the structural features of cyclopropylmethyl, cyclobutyl, and but-3-enyl cations, and was at first assumed to be a non-classical symmetrical cation of the following structure



the so-called "tricyclobutonium" ion, in which all three methylene groups are completely equivalent. In such a cation all the carbon atoms employ ordinary $sp^3$ orbitals for bonding. The three special $sp^3$ orbitals of each methylene group are arranged so that they overlap, as shown above, forming a stable molecular orbital (Fig. 2). The equivalence of the methylene groups in the intermediate cation must inevitably result in an equal probability of isotopic distribution when the reactions are carried out with labelled atoms. In order to demonstrate the mechanism of these reactions, therefore, labelled cyclopropylmethylamine was deaminated. Analysis of the reaction products showed that, although the degree of isotopic redistribution was very large, the methylene groups did not achieve complete equivalence:



In later papers, Roberts and his coworkers[161,162] therefore suggest that the intermediate product in such reactions

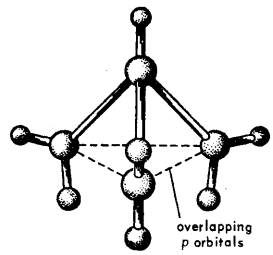
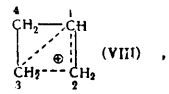



Fig. 2.

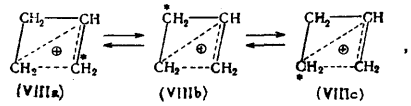
may be an unsymmetrical dicyclic cation of the type VIII, the so-called bicyclobutonium ion



(VIII),

which can be represented geometrically as in Fig. 3.

If the reaction is carried out with a compound containing a labelled methylene group, the existence of three possible labelled bicyclobutonium ions can be represented as follows:



(VIIIa) (VIIIb) (VIIIc),

equilibrium between which is established rapidly but not instantaneously. The less uniform isotopic distribution when the reaction between cyclobutanol and thionyl chloride is carried out in the presence of butylamine in ethereal solution shows that this medium does not favour the establishment of equilibrium. Under better ionisation conditions, equilibrium is reached more rapidly, and this is shown in a more uniform isotopic distribution.

Closer consideration of these structures showed that VIIIa and VIIIb can readily change one into the other, whereas the reversible conversion of VIIIa and VIIIb into VIIIc is difficult. It is possible that the reversible interconversion of the ions VIIIb and VIIIc involves the intermediate formation of the pyramidal tricyclobutonium cation.

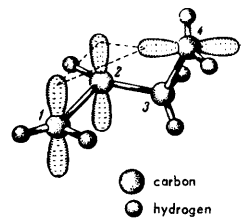
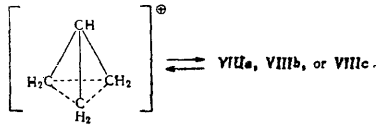



Fig. 3.

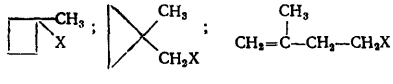
Since this is symmetrical, it can pass with equal ease into VIIIa, VIIIb, or VIIIc:



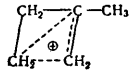
Thus the tricyclobutonium cation can be regarded as a possible intermediate in internal rearrangements.

Roberts' work agrees well with the views of Winstein and his coworkers on intramolecular rearrangements in allyl derivatives [166,167]. Thus the latter workers postulate the possibility of a common intermediate compound in the solvolysis and intramolecular rearrangement of 1,2-dimethylallyl chloride.

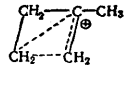
In the bicyclobutonium ion (VIII) the positive charge is distributed among the positions 1–3. On attack by a nucleophilic reagent in these positions, cyclobutyl, cyclopropylmethyl, and but-3-enyl compounds are formed respectively. The proportions of these products in irreversible carbonium-ion reactions led Roberts and his coworkers to the conclusion that the positive charge in VIII is equally distributed among $C_{(1)}$, $C_{(2)}$, and $C_{(3)}$. It was assumed, however, that any disturbance of this balance, produced, for example, by substitution of a methyl group in one of these positions, might lead to profound changes [163–165]. Examination of systems of the type



showed that in this case the intermediate compound is no longer a cation of the type



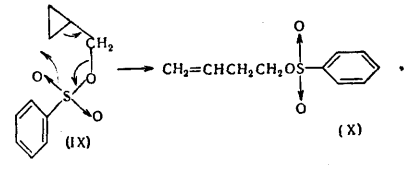
but the non-classical cation



in which the positive charge is no longer completely delocalised, the ion being preferentially located at the tertiary carbon atom. Work on these lines is still being continued by the same investigators.

Several other workers, besides Roberts and his collaborators, have investigated the mechanism of isomerisation, and the views held by the various investigators have not always coincided with those discussed above. Thus in 1952 Brown and Borkowski [168] prepared cyclopropylmethyl chloride by the liquid-phase chlorination of methylcyclopropane, and determined its rate of solvolysis in 80% ethanol. The products thus obtained were not examined, and the reaction was classified as of the first order. These workers cast doubt on the possibility of solvolysis being accompanied by other reactions, as had been found earlier by Roberts.

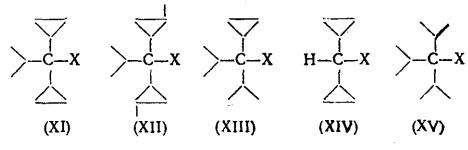
Almost simultaneously Bergstrom and Siegel [169] found that pure cyclopropylmethyl ethyl ether is formed in the solvolysis of cyclopropylmethyl benzenesulphonate (IX) in absolute alcohol. They also found that, on treatment with anhydrous potassium carbonate at 20° for 24 h, the sulphonate is 90% isomerised into a mixture comprising mainly but-3-enyl benzenesulphonate (X). These workers assumed that X can be formed by intramolecular rearrangement as follows:



On the basis of these results, which agreed well with Brown's observations quoted above, the latter completely rejected [170] the mechanism of solvolysis suggested by Roberts and Mazur. In his opinion the solvolysis of cyclopropylmethyl derivatives is not accompanied by rearrangement with intermediate formation of a classical carbonium ion. The products of rearrangement isolated by Roberts and Mazur [157] arose, in Brown's view, because the chloride used was impure.

The isomerisation of cyclopropylmethyl benzenesulphonate (IX) has recently been examined afresh by Denney and Kupchik [171] using $^{18}O$, and these workers completely reject Bergstrom and Siegel's mechanism.

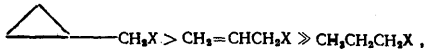
In connection with Brown's work, Caserio *et al.* [162] repeated in 1960 the earlier experiments of Roberts and Mazur [157], using nuclear magnetic resonance spectra to study isotopic distribution, and gas–liquid chromatography to analyse the products of solvolysis. The earlier results were fully confirmed, which casts doubt on Brown's data, and gives grounds for concluding that the mechanism of carbonium-ion reactions suggested by Roberts is the most plausible.



where X represents (a) OH, (b) $p$-$OCOC_6H_4NO_2$, (c) $OCH_3$.

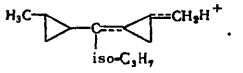
Hart and Sandri [172] published an interesting paper on the solvolysis of the $p$-nitrobenzoates of various cyclopropylcarbinols, their aim being to find out why the rate of solvolysis of cyclopropylmethyl derivatives is greater than that of the corresponding allyl compounds. They were also interested in the behaviour of tertiary systems in this reaction, since until then solvolysis had been studied only with primary and secondary compounds. For this purpose they synthesised the $p$-nitrobenzoates of the series of carbinols XIa–XVa, and subjected them to solvolysis in aqueous or methanolic dioxan solution at various temperatures. The rate of solvolysis was determined by titration of the $p$-nitrobenzoic acid liberated. For solvolysis in 80% aqueous dioxan at 60° the following relative rates were obtained: XVb 1, XIVb 60.7, XIIIb 246, XIb 23 500, and XIIb 124 000.

These workers consider that the reason for the greater rate of solvolysis of cyclopropylmethyl compared with the corresponding allyl derivatives:

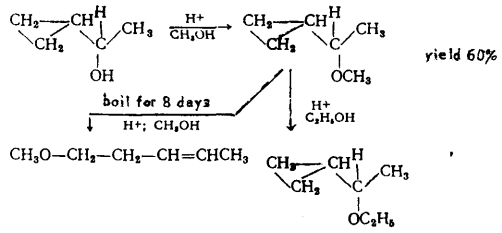


is that the positive charge remaining on the carbon when X is ionised is retained better by the cyclopropyl than by the vinyl group. According to their results, the rate of solvolysis increases on replacement of an isopropyl by a cyclopropyl group, a second three-membered ring increasing the rate to almost the same extent as the first.

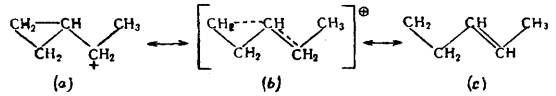
Two methyl substituents in the cyclopropyl group increase the rate of solvolysis fivefold. This increase is too great to be an inductive effect transmitted through the saturated bonds to the tertiary carbon atom in XIIb. Hart and Sandri therefore explain this effect by hyperconjugation involving the three-membered ring, and represent the transmission of the induction effect through the ring thus:



The behaviour of cyclopropylmethylcarbinol in carbonium-ion reactions has been described by Pearson and Langer[173], who carried out a series of reactions based on the scheme:



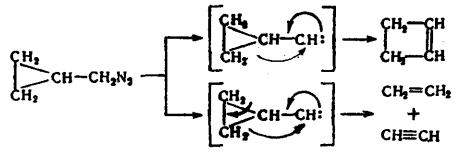

and found that no rearrangement occurred in cyclobutane derivatives. Formation of the allyl derivative required quite severe conditions. These workers explain their results, and also those reported earlier by Dem'yanov[174] and by Bruylants[155], by the intermediate formation of a carbonium ion (*b*):




The severe conditions required for the conversion of a cyclopropylmethyl into an allyl derivative indicate, in the opinion of Pearson and Langer, that the resonance form (*b*) is present to only a small extent, because the positive charge in (*b*) is located on a primary carbon atom.

New rearrangements, leading to the interconversion of cyclopropane and cyclobutane derivatives, have been reported quite recently by Friedman and Shechter[175], who studied the decomposition of diazohydrocarbons to carbenes. These workers[176] had previously found, as had also Powell and Whiting[177], that tosylhydrazones of aliphatic aldehydes and ketones react with alkalis in aprotic solvents to form diazo-compounds, which are able to undergo thermal decomposition to carbenes with loss of nitrogen and formation of olefinic and cyclopropane compounds.

On application of this reaction to cyclopropanal tosylhydrazone (*p*-tolylsulphonylhydrazone), the cyclopropyldiazomethane resulting from reaction of this substance with sodium methoxide in diethyl Carbitol (3,6,9-trioxaundecane) or *N*-methylpyrrolidine at 180° is converted with ring enlargement into cyclobutene (60 or 67%), with disruption of the carbon skeleton into ethylene (13 or 10%) and acetylene (13 or 10%), and with opening of the ring into buta-1,3-diene (4.5 or 7%):

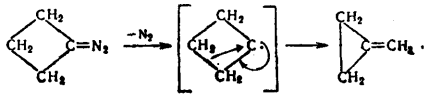


Whether the butadiene is formed directly by decomposition of the tosylhydrazone or as a result of decomposition of the cyclobutene was not established. According to these observations, methylenecyclopropane is not formed at all.

The formation of cyclobutene in this reaction is the first example of rearrangement of a carbon skeleton involving expansion of the ring in a simple carbene system.

The ability of cyclopropylcarbene systems to undergo rearrangement with ring enlargement was confirmed in the reaction of the tosylhydrazone of cyclopropyl methyl ketone in diethyl Carbitol in the presence of alkali, when the products were 1-methylcyclobutene (in 92% yield), vinylcyclopropane (1%), isoprene (2%), propyne (2%), and ethylene (3%).

The decomposition of cyclobutanone tosylhydrazone in diethyl Carbitol or in *N*-methylpyrrolidine to give a carbene involves contraction of the ring, giving methylenecyclopropane (79 or 80%), migration of hydrogen forming cyclobutene (18 or 20%), and also buta-1,3-diene (2–1%):



The decomposition of cyclopentanone tosylhydrazone gives a 94% yield of the normal reaction product, cyclopentene.

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The published information surveyed above is evidence of the extreme instability in many chemical reactions of a cyclobutane ring containing functional groups.

The interest of these isomeric changes lies especially in the fact that the strained four-membered ring passes easily not only into the unstrained five- and six-membered rings but also into the more strained three-membered ring as well as into open-chain derivatives. Thus various reactions described above are often common to cyclopropane and cyclobutane derivatives. It is for this reason that in most cases investigators are interested in both series of compounds, *i.e.* in the whole field of small rings.

From a comparison of the information on the isomeric changes in hydrocarbons and in derivatives of the cyclobutane series, it can be concluded that, in the case of the hydrocarbons, by no means all questions have been exhausted whose solution could shed additional light on isomeric changes in three- and four-membered rings.

1. E.Vogel, Fortschr.chem.Forsch., 3, 430 (1955).
2. E.Vogel, Angew.Chem., 72, 4 (1960).
3. I.L.Knunyants, B.L.Dyatkin, and N.P.Gambaryan, Uspekhi Khim., 25, 785 (1956).
4. Ya.L.Gol'dfarb and L.I.Belen'kii, Uspekhi Khim., 29, 470 (1960) [Russ.Chem.Rev., 214 (1960)].
5. V.I.Kuznetsov, "Vozniknovenie Khimii Alitsiklicheskikh Soedinenii" (Development of the Chemistry of Alicyclic Compounds), Moscow, 1961.
6. W.H.Perkin, Jnr., J.Chem.Soc., 51, 1 (1887).
7. T.Curtius, J.prakt.Chem., [ii], 94, 342 (1916).
8. A.W.Dox and L.Yoder, J.Amer.Chem.Soc., 43, 680 (1921).
9. J.P.Wibaut, H.Hoog, S.L.Langedijk, J.Overhoff, and J.Smittenberg, Rec.Trav.chim., 58, 363 (1939).
10. G.B.Heisig, J.Amer.Chem.Soc., 63, 1698 (1941).
11. G.B.Heisig and F.H.Stodola, Org.Synth., 23, 16 (1943).
12. N.M.Kizhner, Zhur.Russ.Fiz.-Khim.Obshch., 37, 507 (1905).
13. V.P.Gol'mov and B.A.Kazanskii, Dokl.Akad.Nauk SSSR, 33, 37 (1941).
14. V.P.Gol'mov, Zhur.Obshch.Khim., 19, 1679 (1949).
15. J.Cason and C.F.Allen, J.Org.Chem., 14, 1036 (1949).
16. R.P.Mariella and R.Raube, Bol.Col.quim., Puerto Rico, 8, 24, 32 (1951).
17. R.P.Mariella and R.Raube, Org.Synth., 33, 23 (1953).
18. H.M.Walborsky, J.Amer.Chem.Soc., 71, 2941 (1949).
19. R.P.Linstead and H.N.Rydon, J.Chem.Soc., 582 (1933).
20. A.Campbell and H.N.Rydon, J.Chem.Soc., 3002 (1953).
21. T.A.Favorskaya and I.P.Yakovlev, Zhur.Obshch.Khim., 22, 122 (1952).
22. V.N.Ipat'ev, Zhur.Russ.Fiz.-Khim.Obshch., 30, 391 (1898); 31, 349 (1899); 34, 355 (1902).
23. B.A.Kazanskii and M.Yu.Lukina, Dokl.Akad.Nauk SSSR, 83, 693 (1952).
24. B.A.Kazanskii and M.Yu.Lukina, Izv.Akad.Nauk SSSR, Otd. Khim.Nauk, 47 (1951); 314 (1952); 173 (1954).
25. B.A.Kazanskii and M.Yu.Lukina, Dokl.Akad.Nauk SSSR, 94, 887 (1954).
26. S.F.Marrian, Chem.Rev., 43, 149 (1948).
27. G.G.Gustavson, J.prakt.Chem., [ii], 54, 97, 104 (1896); [ii], 56, 93 (1897).
28. Org.Synth.(Translated into Russian), 2, 443 (1949).
29. J.M.Conia, P.Leriverend, and J.L.Rippol, Bull.Soc.chim. France, 1803 (1961).
30. J.M.Derfer, K.W.Greenlee, and C.E.Boord, J.Amer.Chem. Soc., 67, 1863 (1945).
31. J.M.Derfer, K.W.Greenlee, and C.E.Boord, J.Amer. Chem.Soc., 71, 175 (1949).
32. J.D.Roberts and C.W.Sauer, J.Amer.Chem.Soc., 71, 3925 (1949).
33. S.V.Lebedev, Zhur.Russ.Fiz.-Khim.Obshch., 43, 820 (1911).
34. S.V.Lebedev and B.K.Merezhkovskii, Zhur.Russ.Fiz.--Khim.Obshch., 45, 1925 (1913).
35. A.T.Blomquist and J.A.Verdol, J.Amer.Chem.Soc., 78, 109 (1956).
36. K.Alder and O.Ackermann, Chem.Ber., 90, 1697 (1957).
37. H.N.Cripps, J.K.Williams, and W.H.Sharkey, J.Amer. Chem.Soc., 80, 751 (1958).
38. H.N.Cripps, J.K.Williams, and W.H.Sharkey, J.Amer. Chem.Soc., 81, 2723 (1959).
39. F.F.Caserio, Jnr., S.H.Parker, R.Piccolini, and J.D.Roberts, J.Amer.Chem.Soc., 80, 5507 (1958).
40. J.K.Williams and W.H.Sharkey, J.Amer.Chem.Soc., 81, 4269 (1959).
41. H.N.Cripps, J.K.Williams, V.Tullio, and W.H.Sharkey, J.Amer.Chem.Soc., 81, 4904 (1959).
42. H.Staudinger, "Die Ketene", Verlag Enke, Stuttgart, 1912.
43. E.R.Buchman, J.C.Conly, D.H.Deutsch, W.G.Finnegan, G.L.Fujimoto, H.L.Herzog, D.R.Howton, M.Madoff, and H.M.Walborsky, Technical Reports Calif.Inst. of Technol., 1951.
44. E.R.Buchman and H.L.Herzog, J.Org.Chem., 16, 99 (1951).
45. H.Staudinger and E.Suter, Ber., 53, 1092 (1920).
46. H.Staudinger, Helv.Chim.Acta, 7, 19 (1924).
47. E.Vogel and K.Müller, Annalen, 615, 29 (1958).
48. P.Lipp and R.Köster, Ber., 64, 2823 (1931).
49. D.A.Semenow, E.F.Cox, and J.D.Roberts, J.Amer.Chem. Soc., 78, 3221 (1956).
50. S.Kaarsemaker and J.Coops, Rec.Trav.chim., 70, 1033 (1951).
51. R.Willstätter and J.Bruce, Ber., 40, 3982 (1907).
52. J.Cason and R.L.Way, J.Org.Chem., 14, 31 (1949).
53. P.Pommerantz, A.Fookson, T.W.Mears, S.Rothberg, and F.L.Howard, J.Res.Nat.Bur.Stand., 52, 59 (1954).
54. M.D.Owen, G.R.Ramage, and J.L.Simonsen, J.Chem. Soc., 1211 (1938).
55. R.Ya.Levina, M.G.Kuz'min, and Yu.S.Shabarov, Vestnik Moskov.Univ., No.1, 170 (1957).
56. Yu.S.Shabarov, N.I.Vasil'ev, N.K.Mamaeva, and R.Ya.Levina, Dokl.Akad.Nauk SSSR, 135, 879 (1960).
57. R.Ya.Levina, Yu.S.Shabarov, M.G.Kuz'min, N.I.Vasil'ev, and E.G.Treshchova, Dokl.Akad.Nauk SSSR, 121, 303 (1958).
58. R.Ya.Levina, Yu.S.Shabarov, M.G.Kuz'min, N.I.Vasil'ev, S.I.Pokraka, and E.G.Treshchova, Zhur.Obshch.Khim., 29, 3541 (1959).
59. R.Ya.Levina, Yu.S.Shabarov, and M.G.Kuz'min, Dokl. Akad.Nauk SSSR, 127, 111 (1959).
60. M.Yu.Lukina, Uspekhi Khim., 31, 901 (1962) [Russ.Chem. Rev., 419 (1962)].
61. G.S.Handler and J.H.Aderson, Tetrahedron, 2, 345 (1958).
62. C.A.Coulson and W.E.Moffitt, Phil.Mag., [vii], 40, 1 (1949).
63. J.D.Dunitz and V.Schomaker, J.Chem.Phys., 20, 1703 (1952).
64. G.W.Rathjens, Jnr., N.K.Freeman, W.D.Gwinn, and K.S.Pitzer, J.Amer.Chem.Soc., 75, 5634 (1953).
65. A.Almenningen, O.Bastiansen, and P.N.Skancke, Acta Chem.Scand., 15, 711 (1961).
66. F.H.Seubold, Chem.and Ind., 1389 (1954).
67. G.F.Carter and D.H.Templeton, Acta Cryst., 6, 805 (1953).
68. S.W.Benson, Ind.Eng.Chem., Analyt., 14, 189 (1942).
69. S.Kaarsemaker and J.Coops, Rec.Trav.chim., 71, 261 (1952).
70. G.W.Rathjens, Jnr., and W.D.Gwinn, J.Amer.Chem.Soc., 75, 5629 (1953).
71. M.E.Vol'pin, Uspekhi Khim., 29, 298 (1960) [Russ.Chem. Rev., 129 (1960)].
72. J.M.Derfer, E.E.Pickett, and C.E.Boord, J.Amer.Chem. Soc., 71, 2482 (1949).
73. B.B.Loeffler, E.Eberlin, and L.W.Pickett, J.Chem.Phys., 28, 345 (1958).
74. R.C.Lord and D.G.Rea, J.Amer.Chem.Soc., 79, 2401 (1957).
75. J.J.Wren, J.Chem.Soc., 2208 (1956).
76. V.T.Aleksanyan, M.Yu.Lukina, Kh.E.Sterin, and B.A.Kazanskii, Izv.Akad.Nauk SSSR, Ser.Fiz., 18, 699 (1954).
77. V.T.Aleksanyan, Kh.E.Sterin, M.Yu.Lukina, and L.A.Nakhapetyan, "Materialy X Vsesoyuznogo Soveshchaniya po Spektroskopii" (Proceedings of the Tenth

All-Union Conference on Spectroscopy), Vol.1, 1957, p.68.
78. E.G.Treshchova, Yu.N.Panchenko, N.V.Vasil'ev, M.G.Kuz'min, Yu.S.Shabarov, and R.Ya.Levina, Optika i Spektrosk., 8, 371 (1960).
79. E.R.Buchman and D.R.Howton, J.Amer.Chem.Soc., 70, 2517 (1948).
80. E.R.Buchman and D.R.Howton, J.Amer.Chem.Soc., 70, 3510 (1948).
81. R.C.Krug, L.W.Smith, and C.E.Fry, J.Amer.Chem.Soc., 76, 3222 (1954).
82. D.E.Applequist and J.D.Roberts, J.Amer.Chem.Soc., 78, 874, 4012 (1956).
83. A.T.Blomquist and J.A.Verdol, J.Amer.Chem.Soc., 77, 1807 (1955).
84. W.J.Bailey and H.R.Golden, J.Amer.Chem.Soc., 75, 4780 (1953).
85. Yu.S.Shabarov, N.I.Vasil'ev, and R.Ya.Levina, Zhur. Obshch.Khim., 31, 1812 (1961).
86. C.T.Genaux, F.Kern, and W.D.Walters, J.Amer.Chem. Soc., 75, 6196 (1953).
87. J.Langrish and H.O.Pritchard, J.Phys.Chem., 62, 761 (1958).
88. R.Srinivasan and S.M.E.Kellner, J.Amer.Chem.Soc., 81, 5801 (1959).
89. W.Cooper and W.D.Walters, J.Amer.Chem.Soc., 80, 4220 (1958).
90. R.E.Wellman and W.D.Walters, J.Amer.Chem.Soc., 79, 1542 (1957).
91. M.N.Das and W.D.Walters, Z.phys.Chem.(Frankfurt), 15, 22 (1958).
92. S.M.E.Kellner and W.D.Walters, J.Phys.Chem., 65, 466 (1961).
93. H.R.Gerberich and W.D.Walters, J.Amer.Chem.Soc., 83, 3935 (1961).
94. J.J.Drysdale, H.B.Stevenson, and W.H.Sharkey, J.Amer. Chem.Soc., 81, 4908 (1959).
95. E.Vogel, Annalen, 615, 1 (1958).
96. V.N.Ipat'ev and N.L.Tikhotskii, Zhur.Russ.Fiz.-Khim. Obshch., 36, 760 (1904).
97. O.Filipov, Zhur.Russ.Fiz.-Khim.Obshch., 46, 1197 (1914).
98. M.N.Doyarenko, Zhur.Russ.Fiz.-Khim.Obshch., 48, 1 (1926).
99. N.A.Rozanov, Zhur.Russ.Fiz.-Khim.Obshch., 61, 2297 (1929).
100. M.Yu.Lukina, L.A.Nakhapetyan, V.A.Ovodova, and B.A.Kazanskii, Dokl.Akad.Nauk SSSR, 127, 567 (1959).
101. B.A.Kazanskii, M.Yu.Lukina, L.A.Nakhapetyan, V.T.Aleksanyan, and Kh.E.Sterin, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1421 (1956).
102. B.A.Arbuzov and Z.G.Isaeva, Izv.Akad.Nauk SSSR, Otd. Khim.Nauk, 843 (1953).
103. M.B.Turova-Polyak and M.Yu.Lukina, Zhur.Obshch. Khim., 43, 179 (1948).
104. M.B.Turova-Polyak and N.B.Baranovskaya, Zhur.Obshch. Khim., 9, 429 (1939).
105. M.B.Turova-Polyak and O.I.Polyakova, Zhur.Obshch. Khim., 9, 233 (1939).
106. M.B.Turova-Polyak, N.P.Egorova, and E.N.Petrova, Zhur.Obshch.Khim., 16, 825 (1946).
107. M.B.Turova-Polyak and Z.Manaeva, Zhur.Obshch.Khim., 9, 1279 (1939).
108. M.B.Turova-Polyak and A.F.Koshelev, Zhur.Obshch. Khim., 9, 2179 (1939).
109. M.B.Turova-Polyak and G.A.Tarasova, Zhur.Obshch. Khim., 10, 172 (1940).
110. M.B.Turova-Polyak and T.S.Slovokhotova, Zhur.Obshch. Khim., 10, 1435 (1940).
111. M.B.Turova-Polyak and E.V.Vsevolozhskaya, Zhur. Obshch.Khim., 11, 824 (1941).
112. M.B.Turova-Polyak, I.Gurvich, and N.Egorova, Zhur. Obshch.Khim., 17, 137 (1947).
113. H.Pines, W.D.Huntsman, and V.N.Ipatieff, J.Amer.Chem. Soc., 75, 2315 (1953).
114. V.N.Ipatieff, H.Pines, and B.B.Corson, J.Amer.Chem. Soc., 60, 577 (1938).
115. V.N.Ipatieff, B.B.Corson, and H.Pines, J.Amer.Chem. Soc., 58, 919 (1936).
116. V.N.Ipatieff, H.Pines, and L.Schmerling, J.Amer.Chem. Soc., 60, 353 (1938).
117. R.Willstätter and J.Bruce, Ber., 40, 3979 (1907).
118. S.V.Lebedev, Zhur.Russ.Fiz.-Khim.Obshch., 43, 837 (1911).
119. N.A.Rozanov, Zhur.Russ.Fiz.-Khim.Obshch., 61, 2296 (1929).
120. S.E.Raik, Uch.Zap.Moskov.Gos.Univ., 71, 65 (1941).
121. S.E.Raik, Zhur.Obshch.Khim., 11, 324 (1941).
122. B.A.Kazanskii and T.F.Bulanova, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 29 (1947).
123. B.A.Kazanskii and M.Yu.Lukina, Dokl.Akad.Nauk SSSR, 74, 263 (1950).
124. M.Yu.Lukina, V.A.Ovodova, and B.A.Kazanskii, Dokl. Akad.Nauk SSSR, 97, 683 (1954).
125. B.A.Kazanskii, M.Yu.Lukina, and L.A.Nakhapetyan, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 1274 (1956).
126. B.A.Kazanskii, A.L.Liberman, M.Yu.Lukina, and I.V.Gostunskaya, Khim.Nauka i Prom., 2, 172 (1957).
127. M.Yu.Lukina, S.V.Zotova, and B.A.Kazanskii, Dokl. Akad.Nauk SSSR, 116, 793 (1957).
128. N.M.Kizhner, Zhur.Russ.Fiz.-Khim.Obshch., 37, 509 (1905).
129. N.M.Kizhner, Zhur.Russ.Fiz.-Khim.Obshch., 40, 994 (1908).
130. N.M.Kizhner, Zhur.Russ.Fiz.-Khim.Obshch., 42, 1211 (1910).
131. N.M.Kizhner, Zhur.Russ.Fiz.-Khim.Obshch., 40, 676 (1908).
132. N.M.Kizhner, Zhur.Russ.Fiz.-Khim.Obshch., 37, 517 (1905).
133. N.M.Kizhner, Zhur.Russ.Fiz.-Khim.Obshch., 42, 1227 (1910).
134. G.Chavanne and G.Chiurdoglu, Bull.Soc.chim.belges, 51, 11 (1942).
135. T.A.Favorskaya and I.P.Yakovlev, Zhur.Obshch.Khim., 22, 113 (1952).
136. T.A.Favorskaya and I.P.Yakovlev, Zhur.Obshch.Khim., 22, 122 (1952).
137. T.A.Favorskaya and I.P.Yakovlev, Zhur.Obshch.Khim., 22, 215 (1952).
138. T.A.Favorskaya and I.P.Yakovlev, Zhur.Obshch.Khim., 22, 1816 (1952).
139. N.Ya.Dem'yanov, Zhur.Russ.Fiz.-Khim.Obshch., 42, 837 (1910).
140. G.T.Tatevosyan, M.O.Melikyan, and A.T.Terzyan, Zhur. Obshch.Khim., 17, 981 (1947).
141. B.A.Kazanskii, Zhur.Obshch.Khim., 6, 1598 (1936).
142. H.Pines, W.D.Huntsman, and V.N.Ipatieff, J.Amer.Chem. Soc., 75, 2315 (1953).
143. W.Hückel, W.Tappe, and G.Legutke, Annalen, 543, 191 (1940).
144. B.A.Kazanskii, M.Yu.Lukina, and L.A.Nakhapetyan, Dokl. Akad.Nauk SSSR, 101, 683 (1955).
145. B.A.Kazanskii, M.Yu.Lukina, and L.A.Nakhapetyan, Izv. Akad.Nauk SSSR, Otd.Khim.Nauk, 692 (1957).
146. M.N.Doyarenko, Zhur.Russ.Fiz.-Khim.Obshch., 58, 1, 16, 27 (1926).

147. C.G.Overberger and A.E.Borchert, J.Amer.Chem.Soc., 82, 1007 (1960).
148. N.Ya.Dem'yanov and M.Lushnikov, Zhur.Russ.Fiz.-Khim. Obshch., 35, 26 (1903).
149. N.Ya.Dem'yanov, Ber., 40, 4961 (1907).
150. N.Ya.Dem'yanov, Uspekhi Khim., 3, 493 (1934).
151. W.H.Perkin, Jnr., J.Chem.Soc., 65, 950 (1894).
152. P.Dalle, Bull.Classe Sci., Acad.roy.Belg., 36 (1902).
153. N.Ya.Dem'yanov, Ber., 40, 4393 (1907).
154. L.I.Smith and S.McKenzie, Jnr., J.Org.Chem., 15, 74 (1950).
155. P.Bruylants and A.Dewall, Bull.Classe Sci., Acad.roy. Belg., 14, 140 (1928).
156. T.A.Favorskaya and Sh.A.Fridman, Zhur.Obshch.Khim., 18, 2080 (1948).
157. J.D.Roberts and R.H.Mazur, J.Amer.Chem.Soc., 73, 2509 (1951).
158. J.D.Roberts and W.F.Gorham, J.Amer.Chem.Soc., 74, 2278 (1952).
159. J.D.Roberts and R.H.Mazur, J.Amer.Chem.Soc., 73, 3542 (1951).
160. J.D.Roberts and V.C.Chambers, J.Amer.Chem.Soc., 73, 5034 (1951).
161. R.H.Mazur, W.N.White, D.A.Semenov, C.C.Lee, M.S.Silver, and J.D.Roberts, J.Amer.Chem.Soc., 81, 4390 (1959).
162. M.C.Caserio, W.H.Graham, and J.D.Roberts, Tetrahedron, 11, 171 (1960).
163. E.Renk and J.D.Roberts, J.Amer.Chem.Soc., 83, 878 (1961).
164. E.Renk, P.R.Shafer, W.H.Graham, R.H.Mazur, and J.D.Roberts, J.Amer.Chem.Soc., 83, 1987 (1961).
165. E.F.Cox, M.C.Caserio, M.S.Silver, and J.D.Roberts, J.Amer.Chem.Soc., 83, 2719 (1961).
166. W.G.Young, S.Winstein, and L.Goering, J.Amer.Chem. Soc., 73, 1958 (1951).
167. S.Winstein and A.H.Feinberg, J.Amer.Chem.Soc., 80, 459 (1958).
168. H.C.Brown and M.Borkowski, J.Amer.Chem.Soc., 74, 1894 (1952).
169. C.G.Bergstrom and S.Siegel, J.Amer.Chem.Soc., 74, 145 (1952).
170. H.C.Brown, Falk-Plant Lecture at Columbia University (6th March 1957) and Seminar at Harvard University (10th October 1958): see Tetrahedron, 11, 171 (1960).
171. D.B.Denney and E.J.Kupchik, J.Amer.Chem.Soc., 82, 859 (1960).
172. H.Hart and J.M.Sandri, J.Amer.Chem.Soc., 81, 320 (1959).
173. R.G.Pearson and S.H.Langer, J.Amer.Chem.Soc., 75, 1065 (1963).
174. N.Ya.Dem'yanov and M.N.Doyarenko, Ber., 55, 2718 (1922).
175. L.Friedman and H.Shechter, J.Amer.Chem.Soc., 82, 1002 (1960).
176. L.Friedman and H.Shechter, J.Amer.Chem.Soc., 81, 5512 (1959).
177. J.W.Powell and MC.Whiting, Tetrahedron, 7, 305 (1959).

# MODERN VIEWS ON THE MECHANISM OF THE CATIONIC POLYMERISATION OF VINYL MONOMERS

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## I. INTRODUCTION

Since the basic principles of the theory of cationic polymerisation were laid down in monographs dealing with the general chemistry of polymers [1-5] and in review articles [6-8], in particular Pepper's outstanding review [6], there have been many new publications which have barely found mention in the more recent review literature [9,10]. Moreover, many recent investigations have broadened the earlier concepts and make it necessary to review the existing theories on the mechanism of formation, propagation, and termination of chains in cationic polymerisation. The present review is intended to focus attention on these studies. The existence of the earlier sources (especially Pepper and Plesch [6,8,9]) covering the literature extremely fully makes a long introduction unnecessary here, and we limit ourselves to the following brief notes.

Because of the considerable individuality of each polymerisation system, it is impossible to set out a universal mechanism for cationic polymerisation such as is possible for polymerisation by a radical mechanism. Nevertheless, there are some features of cationic polymerisation which are general. The initiation step can be formulated in terms of equations:

for acid catalysis

$$HX + \overset{|}{C}{=}\overset{|}{C} \rightarrow H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C^+}} + X^-, \qquad (1)$$

for catalytic complexes of the proton-donor–Lewis acid type such as $BF_3.H_2O$

$$H^+[AB]^- + \overset{|}{C}{=}\overset{|}{C} \rightarrow H{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C^+}} + [AB]^-. \qquad (2)$$

and for catalytic complexes of the carbonium ion-donor–Lewis acid type such as $SnCl_4.C_4H_9Cl$

$$R^+[AX^-] + \overset{|}{C}{=}\overset{|}{C} \rightarrow R{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C^+}} + [AX]^-. \qquad (3)$$

The most widely held view is that the monomeric cations formed by one of these reactions and the growing macrocations are not kinetically independent entities, but exist as ion–counterion pairs held together by electrostatic forces. The growth of the chain is then considered as the entry of a monomer molecule into the interaction zone of the components of such pairs:

$$\sim\overset{|}{C^+} + [AB]^- + \overset{|}{C}{=}\overset{|}{C} \rightarrow \sim\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C^+}} + [AB]^-.$$

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