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STRUCTURE AND REACTIVITY OF CYCLOPROPANE AND ITS DERIVATIVES

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I. INTRODUCTION

In certain physical and chemical properties cyclopropane and its derivatives differ markedly from alicyclic compounds with a larger number of carbon atoms in the ring and are more similar to alkenes. The anomalous behaviour of compounds containing a three-membered carbon ring, including their typical unsaturation, has for a long time been interpreted solely by the assumption that considerable strain, in the original Baeyer sense, exists in this ring.

The criterion of unsaturation in organic chemistry is the capacity of a compound to take part in addition reactions. This is certainly characteristic of multiple bonds. The three-membered carbon ring also exhibits unsaturation towards reagents which unite with alkenes. It should, however, be stressed that unsaturation in the cyclopropane series is less pronounced than in alkenes.

The analogy between the three-membered ring and the double bond is clearly brought out in cases where this ring is adjacent to a double bond. In their properties such systems are similar to conjugated ones of the π,π-type rather than to σ,π-systems.

With the accumulation of the experimental evidence for the unsaturation of the three-membered ring it became obvious that the explanation of this property does not reside in strain but in the peculiar electronic structure of cyclopropane. Since 1945, a great deal of work has been devoted to this subject.

There is a series of reviews dealing with the synthesis and properties of cyclopropane derivatives[1-3]. In the present review an effort has been made to present the current views on the structure of cyclopropane and the most interesting work on the reactivity of these compounds, and also to elucidate the reactivity and certain other properties of systems in which the three-membered ring is adjacent to unsaturated groups. Unsaturation, and especially the ability of the three-membered ring to conjugate, can only by understood in terms of the modern concept of the structure of cyclopropane, and are inexplicable in terms of the classical theory.

II. STRUCTURE OF CYCLOPROPANE

Before discussing work on the cyclopropane structure the following well-known facts may usefully be reiterated.

Pauling[4] introduced the theory that bonds are formed in the direction of the greatest concentration of electronic clouds. This allows maximum overlapping of electron clouds derived from two atoms, *i.e.* maximum overlap of the orbitals of the two electrons forming the bond. The electron-pair (covalent) bond is formed through the interaction of two electrons of opposite spins derived from two atoms, forming one stable orbital around them. The valence shell of carbon atom consists of four such stable orbitals, one 2*s* orbital and three 2*p* orbitals. As a result, carbon can form four covalent bonds.

The *s* orbital (Fig. 1) is spherically symmetrical and can form a bond in any direction.

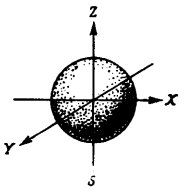


Fig.1.

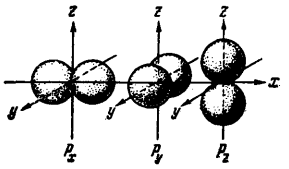


Fig.2.

The three 2*p* orbitals (Fig. 2) are directed along mutually perpendicular axes and form bonds in these directions. In view of the directional property of the *p* orbital, if only its angular distribution is considered, its magnitude will be $\sqrt{3}$ times that of an *s* orbital. The value of the angular contribution to a bonding orbital is termed its "strength"; and is unity for an *s* orbital, 1.732 for a *p* orbital. In other words *p* orbitals can overlap more strongly with the orbitals of another atom than *s* orbitals of the same shell, and bonds formed from *p* orbitals are stronger than those from *s* orbitals†.

However, these orbitals are not employed as such in bonds between two atoms. The orbital used for bonding is formed by linear combination of *s* and *p* orbitals of definite numerical coefficients, and is twice as strong as *s* or *p* orbitals taken separately; it is called a hybrid orbital (Fig. 3).

Strongly concentrated in the direction of the bond, the hybrid orbital is well-adapted for overlapping with the orbital of another atom, and can therefore produce a stronger bond.

In saturated compounds, a carbon atom forms four such hybrid orbitals, mutually inclined at 109°28', that is, directed to the corners of a regular tetrahedron. Such hybridisation, yielding maximum bond energy, is termed sp^3 hybridisation.

In ethylene, carbon atoms are in a state of sp^2 hybridisation. Here, three hybrid orbitals lie in a plane at angles of 120°, and a fourth orbital, which is a pure *p* orbital, has its symmetry axis perpendicular to that plane. This type of hybridisation is termed trigonal.

† This is right if the radial functions of *s* and *p* orbitals are assumed to be equal. Strictly speaking this is not the case in real atoms, and the Pauling theory should therefore be regarded as an approximation.

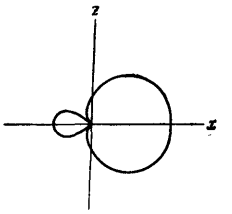


Fig.3.

Cyclopropane, formally a saturated compound, should belong to the type of compound in which the carbon atom is in a state of sp^3 hybridisation. The peculiarity of its structure, however, lies in the fact that the angles between carbon atoms are distorted and are not tetrahedral, which is in contradiction with the strict orientation of sp^3 hybrid orbitals in saturated open-chain carbon compounds. For this reason the structure of cyclopropane could not be interpreted by the Pauling theory of directed bonds and demanded further refinement of that theory.

Duffey was one of the first to study a suitable model for a non-tetrahedral carbon atom[5]. He attempted to calculate the external valence angles in some alicyclic compounds bearing in mind that the internal valency angles are predetermined by the geometry of the molecule. He obtained the value 111°1' for the H–C–H angles in cyclopentane, and 180° for those in cyclobutane and cyclopropane. In the author's own words, these values are only rough approximations. Kilpatrick and Spitzer[6] continued along the same lines of investigation and calculated not only the values of H–C–H angles for several values of C–C–C angles, but also bond strengths in corresponding compounds. They assumed that in compounds with distorted valence angles, the so-called "strained" compounds, the maxima of hybrid orbitals do not necessarily coincide with the direction of the bonds, as postulated by Pauling. Their results are collected in Table 1.

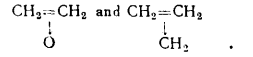
According to Kilpatrick and Spitzer the bond strength is proportional to the value of the orbital in the desired direction, whether or not the maximum of the orbital lies in this direction. When the maximum coincides with the direction of the bond, the bond strength is at its highest (angle 109°28'). In cyclopropane the C–C bond strength is small and differs from that of the C–H bond.

TABLE 1.

C–C bond angle	C–C bond strength	C–H bond angle	C–H bond strength
0°	1.414	126°52'	1.982
60°	1.887	121°58'	1.989
90°	1.984	115°23'	1.995
108°	2.000	109°58'	2.000
109°28'	2.000	109°28'	2.000
120°	1.996	105°50'	1.998
180°	1.932	90°	1.732

This work was very important for the further study of the cyclopropane structure. The applicability of *sp* orbital hybridisation to cyclopropane, with its requirements for strict orientation of four atomic orbitals and location of attached groups along the lines of maximum electron density, was questioned for the first time.

To account for the unsaturation of the three-membered rings Walsh[7] suggested the so-called unsymmetrical π complex formulae for ethylene oxide and cyclopropane, instead of the conventional cyclic ones:

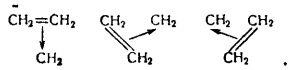


In his opinion two carbon atoms in cyclopropane are in trigonal, and the third in tetrahedral state. He imagines cyclopropane as having a disturbed ethylene structure, where two electrons of the ethylenic bond form bonds with three carbon atoms.

Robinson[8] strongly criticised Walsh's formula for cyclopropane, mainly because it did not reflect the symmetry of the cyclopropane molecule, which is that of an equilateral triangle. Robinson preferred the conventional formula for cyclopropane, and interpreted its peculiar properties by means of quantum mechanical treatment of the linkage of atoms and electron distribution in the molecule.

In his criticism of Walsh's work, McDowell[9] considers that if the double bonds in structures suggested for cyclopropane and ethylene oxide do in fact have the properties ascribed to those bonds, it should be reflected in the Raman spectra of these compounds. However, absorption in the 1600 cm^{-1} region, characteristic of the double bond vibration in ethylene, is absent from both cyclopropane and ethylene oxide.

In reply to these criticisms by McDowell and Robinson, Walsh published another paper[10], in which he contends that the symmetry of the cyclopropane molecule is by no means destroyed if three equivalent resonance formulae are considered:



However, when these are superimposed they are still not equivalent to the classical cyclic formula, since they are based on trigonal, not tetrahedral carbon atoms. As for McDowell's argument, Walsh considers that the ethylene structure is so greatly upset in cyclopropane that its spectra cannot be expected to display frequencies characteristic of the double bond in ethylene. Later on Walsh[11] renounced his formulae for ethylene oxide and cyclopropane, but the basic idea in his work, that the hybridisation of carbon atoms in these compounds resembled that in ethylene, was further developed in his subsequent investigations.

In his second paper Robinson[12] sharply criticised Walsh's concept: in his opinion, the carbon atoms in cyclopropane are not trigonal but tetrahedral, the tetrahedral angles being distorted. A number of publications at that time, mainly reporting experimental data, made possible a more precise representation of the structure of a three-membered ring. Thus, it followed from spectrographic data that cyclopropane molecule is a fully symmetrical planar ring, with the three carbon atoms at the vertices of an equilateral triangle, and the CH_2 planes bisecting the corresponding C–C–C angle in the ring[13].

Assuming that the cyclopropane molecules is built in the form of an equilateral triangle, and that H atoms are located at tetrahedral angles outside the ring plane, Saksena[14] calculated the stretching force constant of the C–C bond as 4.04×10^5 dynes cm^{-1} (a value indicating a weakening of the bond compared with that in ethane), and the stretching force constant of the C–H bond as 4.91×10^5 dynes cm^{-1}, similar to that in ethylene. By cruder methods, Bonner[15] obtained the same value for the C–C stretching force constant. Basing his calculation on infra-red and Raman spectra, Linnett[16] obtained the value 5.05×10^5 dynes cm^{-1} for the C–H stretching force constant in cyclopropane. The stretching force constant of the C–H bond in ethylene[17] is 5.1×10^5 dynes cm^{-1}, and that of the methylene group in paraffins[18] is 4.6×10^5 dynes cm^{-1}. The force constant data thus indicate a similarity between the C–H bonds of cyclopropane and those of ethylene. It was therefore assumed that the H–C–H angle is approximately trigonal, namely 120°, as in alkenes.

These assumptions were confirmed in 1946 by the studies of Bastiansen and Hassel[19] on the electron diffraction of the cyclopropane molecule. The significance of their work is considerable, for they were the first to establish that the H–C–H angle in cyclopropane is 118.2° ± 2°and thus larger than tetrahedral; it is indeed closer to the trigonal (120°) than to the tetrahedral angle (109°28'). These authors also determined the distance between the carbon atoms in cyclopropane as 1.54 Å, and the H–C–C angle as 116.4°.

Somewhat later, Bastiansen and Hassel's data for H–C–H angles in cyclopropane were confirmed by Günthard *et al.*[20], who calculated this angle from infra-red spectra, and by Goldsmith *et al.*[21], who obtained it from the dipole moments of cyclopropane derivatives.

Bastiansen and Hassel's value for the distance between carbon atoms in cyclopropane (1.54 Å) corresponds to that found for alkanes. For this reason Skinner[22] considered that there was very little similarity between the bonds in cyclopropane and double bonds. Nonetheless, thermochemical data indicate a marked weakening of C–C bonds of cyclopropane as compared with diamond and ethane.

At the same period Sugden[23] attempted to apply the method of non-localised molecular orbitals to cyclopropane. He considered CH_2 orbitals as formed by a linear combination of H 1*s* and C 2*s* and $2p_{x,y,z}$ orbitals, and used these for constructing $(CH_2)_3$ orbitals.

The most conclusive evidence that the valence state of carbon atoms with respect to hydrogen in cyclopropane is nearer to sp^2, as it is in ethylene, was obtained from the study of the dipole moment of cyclopropyl chloride. Rogers and Roberts[24] showed that its dipole moment (1.75 *D*) is 0.3 *D* below that for isopropyl chloride and cyclopentyl chloride. The low dipole moment of cyclopropyl chloride may be interpreted by assuming that the C atom linked with the chlorine is trigonal. Such an atom has a higher electronegativity in its *p* valency than the tetrahedral one in its sp^3 hybridisation. For that reason vinyl chloride and phenyl chloride have lower dipole moments than the corresponding alkane analogues.

At this time, Murray and Stevenson[25] synthesised spiropentane. Donohue *et al.*[26], by electron diffraction, confirmed the presence of two three-membered, mutually perpendicular rings in the spiropentane molecule, with H–C–H angles of 120° ± 8°.

New data obtained in the above investigations became the basis for considerable generalisations. Therefore it was quite proper that two fundamental studies devoted to the

cyclopropane structure should appear in 1949 by Walsh[27] and by Coulson and Moffitt[28].

Walsh's paper is the further development of his own ideas on cyclopropane structure, discussed above, based on the assumption that the valence state or the hybridisation of carbon atoms in cyclopropane resembles the hybridisation of carbon in ethylene. He considers that the electronic structure of cyclopropane is based on the union of three ethylenic CH_2 bonds. As in ethylene, each carbon atom forms three hybrid sp^2 valencies, which are in one plane and make an angle of 120° with one another, and one pure p valency, having its symmetry axis normal to this plane, as in Fig. 4.

Fig. 5 shows Walsh's representation of the combination of three CH_2 groups in cyclopropane: the molecular orbitals of the hypothetical cyclopropane ring are formed by the mutual overlap of $2p$ orbitals whose symmetry axes lie in the plane of the ring, as well as by the overlap of hybrid sp^2 orbitals, whose symmetry axes also lie in the ring plane. In Fig. 5 the planes AB, CB, and DB of the C–H bonds lie at 90° to the plane of the diagram. According to Walsh the electron distribution in that system is the following: if it assumed that the CH orbitals are localised, but the molecular orbitals, formed by overlapping of the corresponding atomic orbitals (ψ_1, ψ_2, ψ_3) of each carbon in the ring, are non-localised, then according to Mulliken[29] molecular orbitals are given by:

$$\frac{1}{\sqrt{3}}(\psi_1 + \psi_2 + \psi_3), \quad (1)$$

$$\frac{1}{\sqrt{2}}(\psi_1 - \psi_2), \quad (2)$$

$$\frac{1}{\sqrt{6}}(\psi_1 + \psi_2 - 2\psi_3), \quad (3)$$

where (2) and (3) are degenerate orbitals.

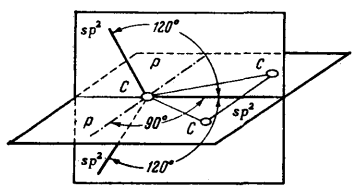


Fig. 4.

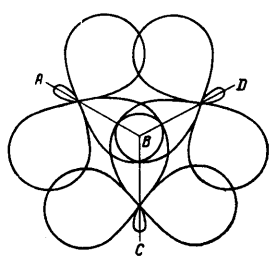


Fig. 5.

Fig. 5 shows two types of overlapping of atomic orbitals. For each type there are three possible molecular orbitals, (1), (2), and (3). In the first type ψ_1, ψ_2, and ψ_3 are hybrid sp^2 orbitals, and in the second they are $2p$ orbitals.

In the type consisting of sp^2 orbitals, (1) will give rise to bonding between carbon nuclei (the bonding orbital), while (2) and (3) are anti-bonding. Of the $2p$ orbitals lying in the plane of the ring, the orbital (1) is anti-bonding and the two degenerate orbitals (2) and (3) are bonding. Here two electrons occupy orbital (1), where ψ_1, ψ_2, and ψ_3 represent hybrid sp^2 orbitals. Their probability pattern is the area a in Fig. 6. Four electrons occupy the two degenerate orbitals (2) and (3), where ψ_1, ψ_2, and ψ_3 represent $2p$ orbitals in the plane of the ring. Their probability pattern is the three-lobed area b,d,e. Walsh points out that in this treatment he assumed non-localised orbitals in the ring but there can also be some localised bond character, and in addition that the overlap between any pair of $2p$ orbitals is neither what it is in the case of a π bond (sideways), nor what it is in a σ bond (endwise). The author himself thus stressed the fact that his treatment of the cyclopropane structure is not sufficiently rigorous.

Nonetheless, the nature of the cyclopropane molecule could be qualitatively understood as formed from three ethylenic CH_2 groups. The resulting orbitals, as shown in Fig. 5, display a certain tendency to form localised bonds in the C–C direction. This structure would account for the stability of cyclopropane, since it is based on three bonding orbitals involving six electrons.

The stability of cyclopropane is in its turn taken to explain the stability of spiropentane and certain other molecules. The most characteristic feature of the overlap of atomic orbitals in cyclopropane is that each carbon atom has a $2p$ orbital with the axis lying in the plane of the ring, and a hybrid orbital directed towards the centre of gravity of the ring. This characteristic must be preserved if one of the carbon atoms changes its state of hybridisation from trigonal to digonal. The hybrid orbital directed towards the centre of the ring must in this case be an sp orbital, two hydrogen atoms must be replaced by another $2p$ orbital with the symmetry axis perpendicular to the plane of the ring, and another sp orbital formed at an angle of 180° with the first. In other words, the second ring must form an angle of 90° with the first (Fig. 7).

The existence of spiropentane, with its two rings at 90° to one another is, in the author's opinion, the most important evidence for the correctness of his views. It should be noted that on classical theory the spiropentane molecule is highly strained.

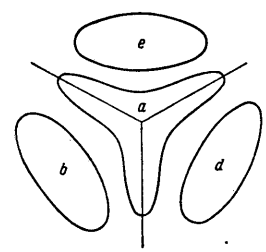


Fig. 6.

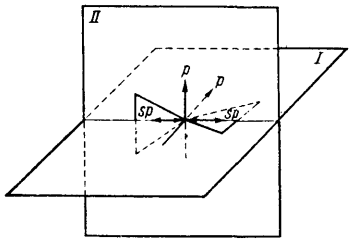


Fig.7.

The characteristic overlap pattern (Fig.5) must be preserved when two carbon atoms change their state of hybridisation from trigonal to digonal. In this case, the $2p$ orbitals, with their axes in the plane of the ring, and the hybrid orbitals directed to the centre of gravity of the ring remain fundamentally as in Fig.5, but each of two carbon atoms should have additional $2p$ orbitals with axes forming an angle of 90° with the plane of the ring. A genuine π bond, and a compound with such structure can in this case be formed:



compounds of this type were later described in a number of papers [30-33].

It should be noted that Walsh's hypothesis on the structure of the three-membered ring is based on much experimental evidence supporting the author's basic idea about the trigonal nature of carbon atoms in cyclopropane. The most important confirmation of this idea, the conjugation of the cyclopropane ring with π bonds, is an indication of the existence of almost pure $2p$ orbitals for the carbon atoms of cyclopropane. Conjugation occurs if there is an overlap of the $2p$ orbital in cyclopropane with the $2p$ orbital in a neighbouring unsaturated group, with their axes parallel to each other.

The positive feature of Walsh's theory is therefore its ability to account for a series of characteristic properties of the three-membered ring, mainly its unsaturation and conjugating capacity.

In this connection mention may be made of the recent publication by Dyatkina and Syrkin [34]. Their view on cyclopropane structure is very close to that of Walsh, but they suggest a somewhat different electron distribution in the molecule (Fig.8).

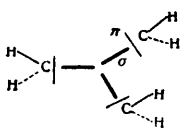


Fig.8.

It is assumed that each cyclopropane carbon atom used two hybrid atomic orbitals to form two C–H bonds. Therefore, for the bonds in the ring there remains one hybrid σ orbital directed from a carbon atom towards the centre of the ring, and a p orbital located in the plane of the ring. The described σ orbitals are fully suited to form ordinary three-centre orbitals of the "central" type. Two lowest orbitals (bonding and anti-bonding) can be occupied by four electrons. The remaining two electrons can occupy the lower one of the three-centre orbitals of the second type, formed from three carbon π orbitals whose axes are located in one plane and form angles of 120° with each other. This is a molecular orbital which overlaps all three carbon atoms along a circumference described around the C–C–C triangle. This interaction is much weaker than the one leading to the formation of a regular three-centre σ orbital of the central type. For this reason only one lower three-centre π orbital seems to be filled.

In the usual model of two-centre σ bonds in cyclopropane, electrons are distributed along the triangular perimeter while in the representation proposed by these authors a considerable part of the electron density appears not in the perimetric region, but inside the triangle, owing to the presence of central three-centre orbitals filled by four electrons.

Conjugation of a cyclopropane ring with double bonds, in their opinion, is caused by the presence of a three-centre π orbital which interacts with the π orbitals of the double bond.

Somewhat later than Dyatkina and Syrkin, Coulson and Moffitt approached the problem of cyclopropane structure from an attitude different from that of Walsh. They first published a short paper [35] in which they elaborated on ideas proposed by Kilpatrick and Spitzer [6] regarding compounds with non-tetrahedral carbon atoms, and briefly presented the results of quantum mechanical calculations of bonds in cyclopropane. Their main work, concerned with the structure and properties of strained hydrocarbons, followed later [28]. They started from the premise that since compounds which possess Baeyer strain do not have tetrahedral valence angles, the hybridisation in these compounds must differ from that found in compounds with undistorted valence angles.

The hybridisation, which is responsible for maximum bond strengths, that is, for the minimum energy in a system, was regarded by these authors as the unknown parameter, which they calculated. They did this bearing in mind a very important fact: since the H–C–H and C–C–C angles in cycloalkanes are different, hybridisations of C–H and C–C bonds in these compounds must also differ. They therefore treated separately the respective hybridisation ratios for C–C and C–H bonds. On the basis of their calculations they arrived at a model of cyclopropane in which each carbon atom is at a vertex of an equilateral triangle and hybridisation is such that two orbitals from any one carbon lie in the plane of the ring forming an angle of ~104° with one another. Less overlapping of orbitals is thus more than compensated by a decrease in strain energy at the carbon atom. Since the C–C bonding orbitals are not directed at one another, the authors describe them as "bent".

According to Coulson and Moffitt's calculations the energy of the system is at a minimum when the H–C–H angle is 116°. This value is in excellent agreement with the experimentally found value for the internal angle in cyclopropane. Results of their calculations for various

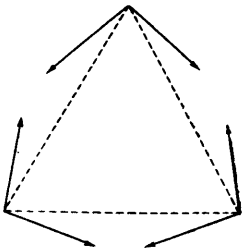


Fig.9.

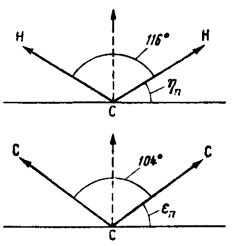


Fig.10.

cycloalkanes and ethylene are collected in Table 2. Values λ and μ in Table 2 are the hybridisation ratios of the C–C and C–H bonds. In order to illustrate their meaning it may by mentioned that by suitably varying μ one can run through the whole range of known types of hybrids: $\mu = 1$, H–C–H = = 180° (digonal); $\mu = \sqrt{2}$, H–C–H = 120° (trigonal); $\mu = \sqrt{3}$, H–C–H = 109°28' (tetrahedral); and $\mu = \infty$, H–C–H = 90° (pure p). The values of angles ϵ_n, η_n, and θ_n given in Table 2, are shown in Fig. 10.

The data of Table 2 show cyclopropane to differ considerably from other hydrocarbons. Thus, λ is considerable higher for the three-membered ring than for cyclobutane or cyclopentane. This indicates the predominantly p character of bonds in this ring (C–C bonds), in contrast to normal tetrahedral bonds, where $\lambda = 1.73$. On the whole, C–H bonds are further away from the p orbital type, which is apparent in the lower value for μ. This effect is less pronounced in cyclobutane, and is completely absent in cyclopentane, where angles and hybridisation are both tetrahedral.

The differences in the hybridisation ratios λ and μ from the mean value 1.73 corresponds to an increase of H–C–H angle, an effect which is slight in cyclobutane but considerable in cyclopropane.

θ is the angle between the direction of the C–C bond and the hybrid orbital. If the hybrid orbital coincides with the direction of the bond $\theta = 0$; here the bonds may be described as direct. If all the bonds are equivalent, as in methane, the angle between them $\pi - 2\epsilon$ is tetrahedral (109°28'). In cycloalkanes, the C–C bonds are strained ($\pi - 2\epsilon \neq 109°28'$) and bent ($\theta \neq 0$). The difference between $E_{(\epsilon,\theta)}$ and $E_{(\epsilon)}$ is a measure of the energy of a strained system.

Judging by the hybridisation ratio μ, C–H bonds in cyclopropane are more akin to those in ethylene than to those in ethane. In cyclobutane they are more like those in ethane or cyclopentane.

Using data from Table 3 the authors drew a curve (Fig. 11) which enables us to predict the force constant for the three cycloalkanes shown at the top of the table. The constants shown in parentheses have been used to draw the curve relating force constant and hybridisation ratio μ.

The values for force constants obtained by Coulson and Moffitt are in good agreement with those given by Linnett [16-17] and Wilson [36] for cyclopropane and cyclobutane.

If the behaviour of C–H bonds with varying hybridisation ratio applies also to C–C bonds, they should be expected to have lower force constants in the strained systems than in normal unstrained (direct) tetrahedral C–C bonds.

In view of the fact that strained bonds are energetically less stable than their unstrained counterparts, their length should be appreciably greater than that in ethane (1.55 Å). However, the investigations mentioned earlier revealed a bond shortening. Coulson and Moffitt think that one should distinguish between internuclear distance and the bond lengths, namely between the length r of the straight line CC and the length of the arc CDC', which is equal to $r\theta \operatorname{cosec}\theta$, and longer than r (Fig.12). When $\theta = 22°$, $\theta \operatorname{cosec}\theta = 1.025$.

This means that the length of the strained (bent) bond may be greater than 1.55 Å, although the internuclear distance between carbon atoms may be less than this. This can easily be understood if hybrid orbitals can be considered to be impenetrable; in this case, the orbitals of an unstrained bond would necessitate a longer interatomic distance than would a strained bond set at an angle (Fig. 13): *i.e.* in the latter case the atoms approach each other more closely than in the former.

Coulson and Moffitt's paper gives contours of equal electron density for strained and unstrained bonds (Fig.14).

As shown in Fig. 14, for strained bonds the lines of equal electron density are distorted. The arrows show the

TABLE 2.

Compound	n	ϵ_n	η_n	θ_n	H H \ C / ($\pi = 2\eta_n$)	λ	μ
Cyclopropane	3	38°	32°	22°	116°	2.03	1.51
Cyclobutane	4	36°	34°30'	9°	111°	1.80	1.67
Cyclopentane	5	35°15'	35°15'	0°	109°30'	1.73	1.73
"Ethylene"	2	40°	28°30'	50°	123°	2.40	1.36

TABLE 3.

Hydrocarbon	H–C–H angle	C–H force constant, dynes cm^{-1}	μ
Cyclopropane	116°	$5.0 \cdot 10^5$	1.51
Cyclobutane	111°	4.85	1.67
Cyclopentane	109.5°	4.8	1.73
Ethane	109.5°	(4.8)	1.73
Ethylene	120°	(5.1)	1.41
Acetylene	180°	(6.0)	1.00
CH radical	90°	(4.1)	—

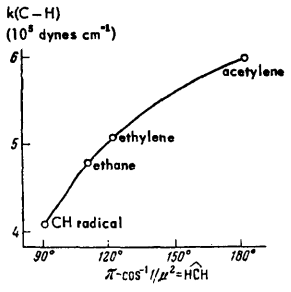


Fig.11.

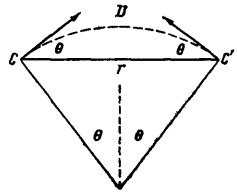


Fig.12.

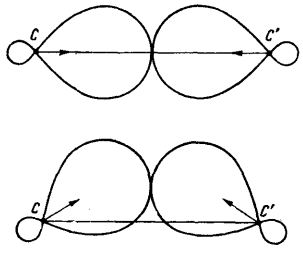


Fig.13.

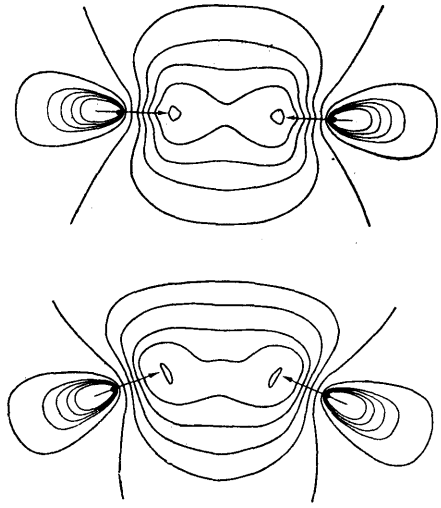


Fig.14.

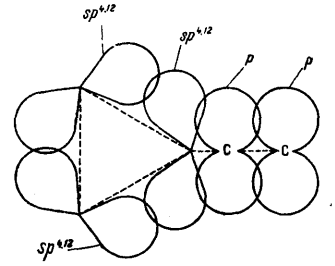


Fig.15.

direction of hybrid orbital maxima. In unstrained bonds these coincide with the direction of the bonds, while in cyclopropane they make an angle $\theta = 60° - 38° = 22°$ with the direction of the bonds. The bent character of the C–C bonds in cyclopropane is demonstrated well here.

Using the Coulson and Moffitt's representation of bent *endo*-orbitals in a three-membered ring Ingraham[37] calculated that these ring orbitals are now $sp^{4.12}$ orbitals instead of the usual tetrahedral sp^3 orbitals formed at a valence angle of 109°28'. The high p character of the *endo*-orbitals results in a high s character of the $sp^{2.28}$ *exo*-bonds in cyclopropane. These bonds are at 116° to each other.

This structure, in Ingraham's opinion, affects the properties of three-membered ring compounds. The most important effect is the result of the fact that these $sp^{4.12}$ bonds are well placed for overlap with adjacent p orbitals of the double bond, as in vinylcyclopropane (Fig. 15).

Cromwell and Graff[38] have a somewhat different concept of the conjugation of similar systems. Taking the ethyleneimine and ethylene oxide rings as examples, they consider conjugation to take place between *endo*-bonds and π bonds, as in Fig. 16.

In this case, to form endocyclic bent bonds in a three-membered ring two carbon atoms use their hybrid orbitals ($2s - 2p\delta$) (angle 104°), while O or N atoms use their $2p_x$ and $2p_y$ orbitals (angle 92°). This type of bond is intermediate between π and σ bonds.

When an atom containing π electrons is linked with a carbon atom from any ring system with bent bonds (ethyleneimine, ethylene oxide, cyclopropane) a degree of interaction or overlap is observed between these bent bonds and the π or p orbitals (see broken lines in Fig. 16).

In conclusion it may be stated that Walsh, and also Coulson and Moffitt interpret the peculiarities of a three-membered ring by a characteristic of the valence state of the ring carbon atoms. In both concepts the valence state or hybridisation is assumed to differ from tetrahedral sp^3. Walsh describes this state as sp^2 hybridisation, but admits

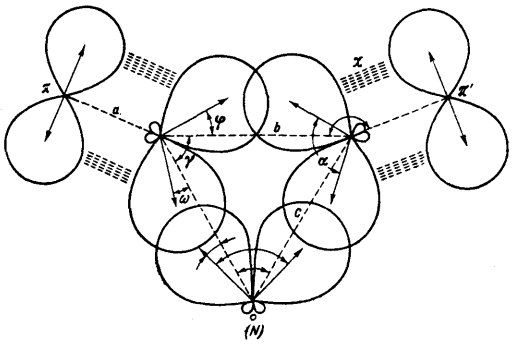


Fig.16.

that it is somewhat of a special type. For example, he assumes a certain amount of localisation of bonds in a three-membered ring.

Coulson and Moffitt's concept of hybridisation in cyclopropane is more concrete. They consider that hybridisation is different for the C–C and the C–H bonds in cyclopropane and that neither is sp^3 or sp^2 hybridisation, which are characteristic of tetrahedral and trigonal carbon atoms, respectively. This means that a new type of bond exists in cyclopropane, different from bonds in saturated molecules and unsaturated ones with undistorted valence angles. In his monograph[39] Coulson termed C–C bonds in cyclopropane "banana" bonds, and this term is gradually gaining ground in the chemical literature.

Although the concept of cyclopropane structure as proposed by Coulson and Moffitt is more rigorous than that of Walsh, they are basically very similar. Thus, although they differ in their description of the endocyclic bonds in cyclopropane, they agree about the delocalisation and the p character of bonding molecular orbitals. It is precisely in terms of these that a series of properties of three-membered rings can easily be understood, in particular their capacity to conjugate with adjacent π bonds.

III. REACTIONS OF CYCLOPROPANE AND ITS DERIVATIVES WITH EMPHASIS ON THE ANALOGY BETWEEN THE THREE-MEMBERED RING AND THE DOUBLE BOND

The characteristic reactivity of the three-membered ring and the deep analogy between the behaviour of cyclopropane derivatives and alkenes can be more readily understood in the light of the above views on cyclopropane structure. Bonds in the three-membered ring differ from those in alkanes or higher alicyclic compounds with undistorted valence angles, their properties resembling more the bonds in alkenes than the σ bonds of saturated compounds. The properties of cyclopropane and its derivatives are therefore understandably dissimilar from those of alkanes or higher alicyclic compounds, and this is no longer to be considered anomalous.

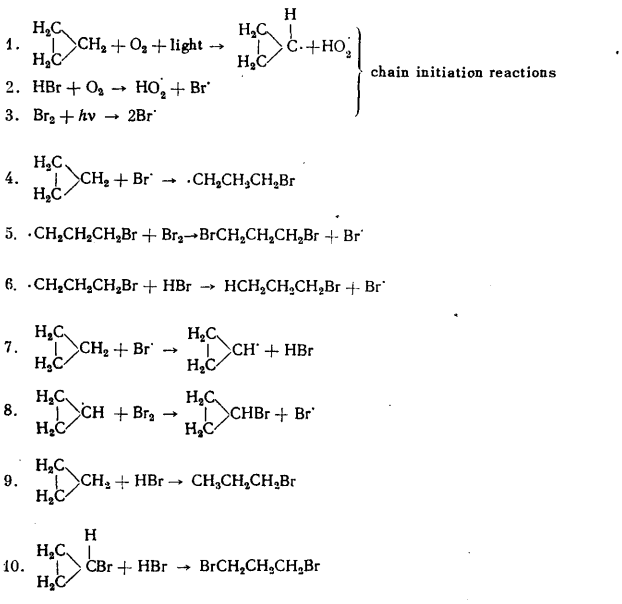
The complex chemistry of cyclopropane has long been attracting the attention of the most prominent Russian and foreign scientists, including Gustavson, Perkin, Willstätter, Kishner, Dem'yanov, Robinson, and others. The literature abounds with data on the reactivity of cyclopropane compounds. The present review deals only with the most interesting reactions which illustrate similarities and discrepancies between the behaviour of a three-membered ring and that of a double carbon–carbon bond. In our opinion these reactions are consistent with the theoretical concepts discussed in the previous section, and can be taken as evidence confirming the hypotheses of Walsh and Coulson and Moffitt on cyclopropane structure.

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The reactions of a three-membered ring with halogens and with hydrogen halides were first studied in 1900 by Gustavson[40]. Ogg and Priest[41] later made a more thorough study of these reactions. They found that at room temperature and in strong light a rapid photochemical reaction took place between cyclopropane and bromine vapour, consisting exclusively of addition to give 1,3-dibromopropane. In the dark, bromine and cyclopropane react only at 220°, but here a considerable amount of substitution occurs as well as the addition.

Ogg and Priest also found that at 250° cyclopropane readily reacts with iodine forming 1,3-diiodopropane. Light has no appreciable effect on this reaction rate. Later, these authors investigated in detail the kinetics of the vapour-phase reaction of cyclopropane and iodine[42].

Kharasch *et al.*[43] made a detailed study of the reaction of cyclopropane with bromine, including the effects of light and oxygen. They found that pure cyclopropane and pure bromine do not react appreciably in the dark, and do so only slightly in light. For that reason they suggested a chain mechanism for bromination, according to the scheme below:



The dots denote unpaired electrons.

The reaction of cyclopropane with chlorine was studied by Gustavson[44], and later in more detail by Stevens[45]. In contrast to bromine and iodine, chlorine is unable to open the three-membered ring, and substitution occurs, mainly forming 1,1-dichlorocyclopropane.

The work by Roberts and Dirstine[46], on the photochemical chlorination of cyclopropane, is of interest. Here also the reaction is slow, and since chlorine attacks hydrogen rather than carbon, results in substitution, not ring-opening. Brown and Borkowski[47] discovered that in the chlorination of methylcyclopropane, despite the presence of a tertiary carbon atom, only the methyl hydrogen atoms undergo substitution.

Freed and Sancier[48] found that, in the temperature range from -43° to -196°, iodine reacts with cyclopropane forming a molecular compound (1 : 1). The composition of the adduct was established from ultra-violet absorption spectra. These authors had earlier obtained similar adducts from a series of alkenes, *e.g.* propene, 2-butenes (*cis* and *trans*), and butadienes. In all cases, the adducts were molecular compounds of molar ratio 1 : 1. The energies of activation were determined.

Ogg and Priest[41] found that cyclopropane is almost completely resistant towards gaseous hydrogen chloride, bromide, and iodide, even at 300°. Freund[49], Gustavson[40], and later Kishner[50], and Kohler and Conant[51], found that cyclopropane and its alkyl derivatives readily react with aqueous solutions of these acids. Alkylcyclopropanes react according to the Markownikow rule, which is evidence in favour of an ionic reaction mechanism. Addition of hydrogen bromide to unsymmetrical alkenes containing alkyl substituents can be represented in the following manner:

$$CH_3-\overset{+\delta}{C}H=\overset{-\delta}{C}H_2+H^+Br^- \rightarrow CH_3-CHBr-CH_3.$$

With alkylcyclopropanes this reaction proceeds as below:

$$CH_3-\overset{+\delta}{\underset{\diagdown\,\diagup}{CH}}-\overset{-\delta}{CH_2}+H^+Br^- \rightarrow CH_3-\underset{Br}{CH}-CH_2-CH_3,$$
$$\qquad\quad CH_2$$

and the cyclopropane ring opens between those carbon atoms which are united with the greatest and the smallest number of alkyl residues, the bromine atom attaching itself to that carbon atom which carries most alkyl radicals. The addition of hydrogen bromide to cyclopropane was studied by Kharasch *et al.*[43] In the presence of an excess of cyclopropane this reaction is greatly accelerated by oxygen, and only slightly by light. In the presence of an equivalent amount of cyclopropane neither oxygen nor light appreciably affect the reaction rate, but an acceleration by peroxides is observed.

Kuivila *et al.*[52] studied the interesting reaction of *N*-bromosuccinimide with 1-phenyl-2-isopropylcyclopropane[53]. This reagent reacts with alkenes to form the corresponding dibromides in good yields. With cyclopropane derivatives, instead of the expected substitution products (isomeric bromides), a small yield of an open-chain dibromide was obtained, formed by ring opening between the two substituted carbon atoms:

$$C_6H_5-\underset{\diagdown\,\diagup}{CH}-\underset{\diagdown\,\diagup}{CH}-\underset{\diagdown\,\diagup}{CH} \xrightarrow{+2\,\begin{matrix}CH_2-CO\\ CH_2-CO\end{matrix}NBr} C_6H_5-\underset{Br}{CH}\ \underset{Br}{CH}-\underset{\diagdown\,\diagup}{CH}$$
$$\qquad\quad CH_2 \quad\ CH_3 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_2 \quad\ CH_3$$
$$\qquad\qquad\quad CH_3 \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_3$$

This reaction is yet another example of the far-reaching analogy between the behaviour of a three-membered ring and a double bond.

One of the most characteristic addition reactions in the cyclopropane series is catalytic hydrogenation involving ring opening (hydrogenolysis).

Although the catalytic hydrogenation of cyclopropane hydrocarbons has been the subject of numerous investigations, it has not been possible until recently to form a clear picture of the conditions and direction of the opening of the three-membered ring in this case.

Willstätter and Bruce[54] found that, over nickel on pumice, cyclopropane undergoes partial hydrogenation at 80°, and is completely hydrogenated at 120°. With the same catalyst, Bond and Sheridan[55] found that hydrogenation commenced at 129°. In the presence of platinum or palladium on pumice, hydrogenation did not start until 50° and 72°, respectively.

Corner and Pease[56] hydrogenated cyclopropane in the presence of nickel on kieselguhr and found that ring opening occurred at 0°. Boeseken and his associates[57] pointed out that the rate of the hydrogenation of cyclopropane over platinum black in acetic acid solution at 25° is the same as that for the hydrogenation of ethylene. On the other hand, Kazanskii *et al.*[58,59] repeatedly observed that in the presence of platinum and palladium blacks in alcoholic solution at room temperature hydrogen does not react with alkylcyclopropanes, while alkenes readily undergo hydrogenation under these conditions. Bond and Sheridan[55] also consider that the hydrogenation of a three-membered ring requires harsher reaction conditions than does the olefinic double bond.

Views also differ as regards the direction of the opening of a three-membered ring on hydrogenation. Rozanov[60] (nickel on asbestos), Kishner[61] (nickel), Kazanskii *et al.*[62,63] (Pt on carbon), and Slabey[64] (platinum oxide) found that alkylcyclopropanes are hydrogenolysed by rupture of the bond between those two ring carbon atoms which carry the greatest number of hydrogen atoms. A different direction of the ring opening was observed by Slobodin *et al.*[65] (Ni on kieselguhr), and by Boord and his coworkers[66,67] (Ni on kieselguhr). They found that, in all the cases studied, the cyclopropane ring was opened at the bond between those two carbon atoms which are united with the greatest and the smallest number of hydrogen atoms.

These contradictory results stimulated Lukina *et al.*[68-70] to undertake a thorough investigation of the behaviour of alkylcyclopropanes under conditions of hydrogenation and they found that in the presence of many substances a three-membered ring readily undergoes isomerisation into open-chain alkenes. This reaction was shown to be caused by carriers used in the preparation of hydrogenation catalysts, particularly silica gel[71], aluminosilicate, kieselguhr, aluminium oxide, and (at relatively higher temperatures) pumice and activated carbon[70]. The result is that, depending on the conditions and the nature of the catalyst, two different reactions proceed concomitantly during the hydrogenation of cyclopropane hydrocarbons: hydrogenolysis, *i.e.*, addition of hydrogen to the three-membered ring, and isomerisation to alkenes, which is followed by the addition of hydrogen to the double bond[68,72,73].

These reactions involve different C–C bonds of the three-membered ring and yield products of different structure.

$$\underset{\diagdown\,\diagup}{R-CH-CH_2} \xrightarrow[H_2]{\text{catalyst}} CH_3-\underset{R}{CH}-CH_3 \qquad \text{hydrogenolysis}$$

$$\underset{\diagdown\,\diagup}{R-CH-CH_2} \xrightarrow[H_2]{\text{catalyst}} R-CH_2-CH_2-CH_3 \qquad \text{isomerisation followed by hydrogenation}$$

The characteristic isomerisation of the three-membered ring under relatively mild conditions has not been taken into account in studies of catalytic hydrogenation so that the two reactions are taken as one, hence the discrepancies as regards the direction of the ring opening and the reaction conditions. In all cases where nickel on kieselguhr was used as a catalyst[65,66,67] the reaction involved mainly or exclusively isomerisation, kieselguhr being very active in catalysing this reaction. The resulting alkene immediately underwent hydrogenation in the presence of nickel, yielding the corresponding alkane. The cleavage of the ring occurred between those two carbon atoms which were united with the greatest and smallest number of hydrogen atoms. This explains the readiness in the opening of the three-membered ring observed by Corner and Pease[56], who used nickel on kieselguhr as hydrogenation catalyst. Direct hydrogenolysis of the ring proceeds readily in the presence of platinum on activated carbon or pumice, since those carriers, at relatively low temperatures used in this reaction, are not very active as isomerising agents. Certain catalysts, for instance palladised carbon[72], catalyse both reactions simultaneously.

Bond and Sheridan[55] studied the kinetics and the mechanism of the hydrogenolysis of cyclopropane in the presence of platinum, palladium, and nickel on pumice. In contrast to alkenes, the hydrogenation of cyclopropane in the 100°–200° temperature range is of first order with respect to cyclopropane, and of zero with respect to hydrogen. This is an evidence that during the hydrogenation of cyclopropane, in the studied range of hydrogen pressure, the catalyst's surface is completely covered by adsorbed hydrogen and the reaction rate is independent of its concentration [in the gas phase (Ed. of Translation)].

Bond and Turkevich[74] studied the deuteration of cyclopropane over platinum and found that the reaction order in this case is the same as in hydrogenation, and depends on temperature. On the basis of their results they dispute the various versions of the mechanism of hydrogenolysis suggested earlier by Bond and Sheridan[55]. In their opinion[74] the most probable mechanism is that whereby a molecule of gaseous cyclopropane unites with two hydrogen atoms after an intermediate formation of an adsorbed radical. The mechanism whereby cyclopropane is first isomerised to propene is excluded, since according to Bond and Turkevich the distribution of deuterium in the propane from the catalytic deuteration of propene differs from that in the propane formed from cyclopropane[74].

The reaction of cyclopropane with deuterium over palladium was studied by Addy and Bond[75]. Hydrogenation of cyclopropane in the presence of platinum and palladium proceed according to the same mechanism, although platinum is more active.

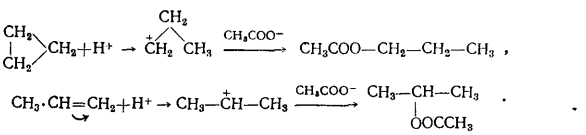
Addy and Bond[76] established that the hydrogenation of cyclopropane in the presence of rhodium and iridium catalysts follows the same reaction mechanism as in the case of platinum or palladium.

In their study of the hydrogenation of cyclopropane in the presence of commercial nickel–aluminosilicate catalyst at 75°, Benson and Kwan[77] obtained a kinetic equation different from that proposed by Bond and Sheridan[55]. Irrespective of that, they believe that the reaction mechanism proposed by Bond and Sheridan is correct. The validity of their results may be questioned, as they studied the isomerisation of cyclopropane into propene under the action of the aluminosilicate carrier, and not its hydrogenolysis. In the presence of nickel, propene undergoes hydrogenation to propane. Hayes and Taylor[78] described the same reaction in the presence of a catalyst prepared by melting magnetite ore with potash, which they termed Fe-catalyst. In this case both the kinetic equation and the suggested reaction mechanism differ from that given by Bond and Sheridan. The authors interpret this by the lower activity of Fe-catalyst in the hydrogenation of cyclopropane owing to the fact that its surface is incompletely covered by hydrogen. The remaining free surface, in their opinion, catalyses the isomerisation of cyclopropane.

Hydrogenolysis is specific not only for a three-membered, but also for four- and five-membered rings. It is only natural to suppose that in the cyclopropane series it should proceed under milder conditions. It is nevertheless difficult to form a clear picture from the literature regarding the differences in the stability of various rings in this reaction.

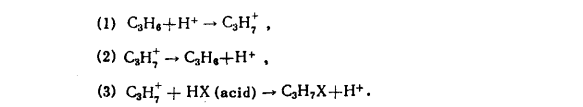
Comparative hydrogenolysis of three hydrocarbons of molecular formula C_5H_{10}, containing different rings, was studied by Lukina *et al.*[79] In the presence of platinised carbon of low activity ethylcyclopropane is completely converted into the corresponding alkane at 50°, methylcyclobutane is hydrogenated on this only at 250°, while with cyclopentane at 250° only the breaking of the carbon–carbon bonds is beginning.

No less interesting are the reactions in which the three-membered ring, like an alkene, may be represented as a nucleophilic reagent. For instance the reaction of cyclopropane with acids, studied for many examples, belongs to this category. Thus, Dorris and Sowa[80] established that cyclopropane reacts with acetic acid in the presence of boron fluoride forming 65% n-propyl acetate. Under the same conditions propene yields the isopropyl ester. The authors suggested the following scheme for those two reactions:



Like the lower alkenes, cyclopropane is absorbed by concentrated sulphuric acid to form esters. Davis and Schuler[81], and later Rathman[82], studied the absorption rate of cyclopropane and propene. Sulphuric acid absorbs cyclopropane more rapidly than propene, the absorption rate depending on acid concentration. Rathman based his method for analysing mixtures of alkenes and cyclopropane on this difference in the absorption rate.

Somewhat later Lawrence and Tipper[83] studied the reactions of cyclopropane and propene with various acids and found that the kinetics are similar in both cases although the reaction rate is different. The authors interpret this as indicating similar reaction mechanisms represented as follows:



It can be assumed that reaction (1) is slow, reaction (2) very rapid, and reaction (3) moderately rapid. The first reaction stage, the addition of a proton, proposed by

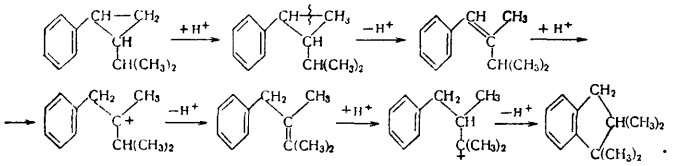
Dorris and Sowa[80], proceeds as shown above. The rate is five times faster for cyclopropane than for propene, which in agreement with the above scheme, is interpreted by the fact that proton can attack any one of the three equivalent carbon atoms in cyclopropane, and only one in propene.

Almost all the investigations of the reactivity of the three-membered ring include comparative studies of the behaviour of cyclopropane derivatives and alkenes of analogous structure. Thus, Davidson and Feldman[84] studied the action of sulphuric acid on monophenylalkenes and monophenylcyclopropanes. Under the conditions employed, alkenes either undergo polymerisation or form indanes and tetralins.

By the action of 90% sulphuric acid 2-isopropyl-1-phenylcyclopropane forms small amounts of 1,1,2-trimethylindane, while 2-methyl-1-phenyl- and 2-ethyl-1-phenyl-cyclopropane form resinous polymers and traces of volatile oils.

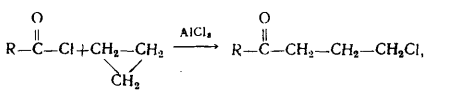
In the opinion of the authors, the attack of sulphuric acid on a 2-alkyl-1-phenylcyclopropane starts by the opening of the cyclopropane ring following the addition of a proton to the least substituted carbon atom. As in the case of alkenes, the resulting carbonium ion may subsequently undergo the following specific reactions: addition to an unsaturated molecule (polymerisation), decomposition to form other carbonium ions or unsaturated compounds with a smaller number of carbon atoms (depolymerisation), isomerisation into other carbonium ions (rearrangement), or decomposition into an alkene and a proton.

These authors found that these reaction types only proceed in the case of isopropyl derivatives, where the conditions for cyclisation are especially favourable. In other cases only polymerisation takes place:



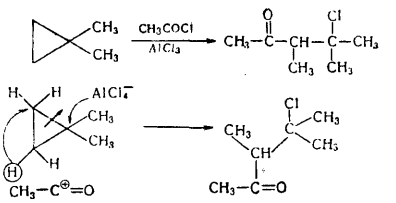
Similar behaviour of the three-membered ring and the double bond has been confirmed by Hart and Curtis[85] in a study of the reaction of cyclopropane with $RCOCl.AlCl_3$ in chloroform (a reaction catalysed by a Lewis acid). Similar reaction with alkenes yields β-chloro-ketones.

Cyclopropane and an acyl halide were expected to form a γ-halogeno-ketone:



where R = CH_3; C_2H_5; C_3H_7; i-C_3H_7; Δ; C_6H_5. This reaction course is probable since the reverse reaction, cyclisation of β-chloro-ketones in the presence of alkali, yields cyclopropyl ketones. In fact, the reaction was accompanied by unexpected rearrangement leading to a mixture of products consisting mainly of the β-chloro-ketone $RCOCH(CH_3)CH_2Cl$ and to a lesser extent of the γ-chloro-ketone $RCOCH_2CH_2CH_2Cl$.

Hart and Levitt[86] studied this reaction with a series of other compounds, and each time they obtained β-chloro-ketones. Using dimethylcyclopropane as an example, they suggested the following reaction mechanism:

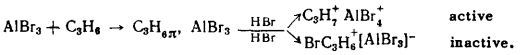


A great deal of work has been done on the action of aluminium halides on the three-membered ring, and a close analogy in the behaviour of alkenes and cyclopropane derivatives was observed.

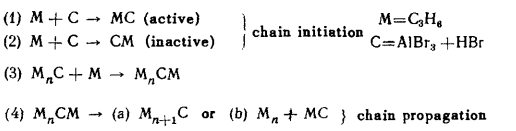
Schmerling[87] alkylated benzene by passing cyclopropane into a solution of aluminium chloride in nitromethane and benzene at 20°–50°. The reaction product was n-propylbenzene. Later, Tipper and Walker[88] studied the kinetics of this reaction.

In 1953 Ipatieff *et al.* studied the reaction of cyclopropane hydrocarbons with aluminium chloride[89]. They found that under their conditions cyclopropane homologues underwent polymerisation. They interpreted this by invoking the olefinic character of the three-membered ring.

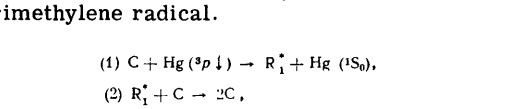
According to Tipper and Walker[90] cyclopropane polymerises in the presence of aluminium bromide and hydrogen bromide (in heptane solution), from 0° to -78°, forming polymers of low molecular weight. These polymers, whose molecular weight is inversely proportional to temperature, appear to be long-chain alkenes with a terminal double bond. The proposed reaction mechanism consists of the initial interaction of cyclopropane, aluminium bromide, and hydrogen bromide leading to two complexes, one of which initiates the reaction, while the other, which is inactive, forms a precipitate:



The first step may possibly consist of complex formation. The mechanism can be represented as follows:

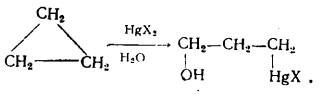


In their study of cyclopropane spectra, Harris *et al.*[91] observed that cyclopropane polymerised on irradiation by ultra-violet light. The polymer is a colourless oil of high boiling point. Gunning and Steacie[92] later made a thorough study of this phenomenon and suggested a mechanism for it which is based on the preliminary formation of an energy-rich trimethylene radical.

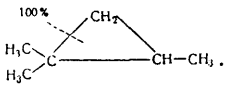


Breaking of the chain takes place when the polymer biradical is no longer able to supply energy for the cleavage of the C–C bond of cyclopropane. In that case the radical is stabilised by a proton shift. Reaction (2) is 43 times faster than reaction (3)‡.

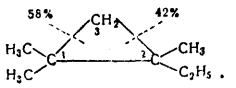
Of considerable interest is the reaction of a three-membered ring with mercuric salts, investigated by Levina and coworkers[93]. Mercuric salts are known to react with the double bond of many alkenes[94] and alkadienes[95]. Cyclopropane hydrocarbons readily react (usually on shaking at room temperature) with mercuric salts at the point where the ring is normally opened, forming γ-hydroxyalkylmercury salts, *i.e.* alcohols mercurated in the γ position:



The three-membered ring in substituted cyclopropane always opens at the bond lying between the two carbon atoms which carry the smallest and the largest number of hydrogen atoms[96]:



If two bonds are equivalent in this respect, a mixture of both possible reaction products is obtained:

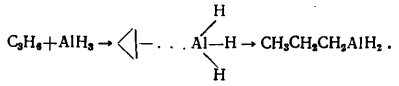


Formation of a somewhat greater amount of the product resulting from the cleavage of the 1–3 bond is accounted for by greater polarisation of that bond as compared with the 2–3 bond[97]. There can be no preliminary isomerisation of the three-membered ring, for then acetate would attach itself at the double bond forming a β-hydroxyalkylmercury acetate. This reaction has been studied so frequently that it could be used for the identification of cyclopropane hydrocarbons.

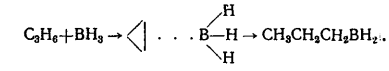
According to Tipper[98], cyclopropane (liquid), in contrast to alkenes, does not form complexes with silver, copper, and mercury salts at low temperatures. Nevertheless, with chloroplatinic acid in acetic anhydride it forms a brown precipitate of the complex $(PtCl_2C_3H_6)_2$. A cold aqueous solution of potassium cyanide decomposes this complex, rapidly liberating cyclopropane. This is evidence that the three-membered ring remains unchanged in the complex. Under these conditions alkenes also form complexes with chloroplatinic acid. Formation of complexes may be taken as evidence supporting the views of Walsh and of Coulson and Moffitt on the unsaturated character of the three-membered ring.

‡ See, however, K.Ivin, J.Chem.Soc., 2241 (1956), in which an alternative mechanism is proposed (Ed. of Translation).

The work by Tipper and Walker[99] on the reaction of cyclopropane with lithium hydroaluminate is also of interest. This reagent reacts with lower alkenes forming the corresponding alkylaluminium compounds. Cyclopropane similarly yields tri-n-propylaluminium. The authors think that the first stage of this reaction consists of the coordination of cyclopropane with AlH_3, which is followed by the shift of hydrogen and the opening of the ring:



This process is subsequently repeated and the reaction results in tri-n-propylaluminium. Graham and Stone similarly observed the formation of a carbon–boron bond in the reaction of cyclopropane with diborane at 80°–100°.[100] Reactions of that type, involving a shift of hydrogen, also take place with alkenes. The authors consider that the "banana" bonds of cyclopropane possess sufficient electron density to permit a reaction of this type:



Graham and Stone consider that the addition of BH_3 or AlH_3 to cyclopropane proceeds through the intermediate formation of a π complex, similar to that formed by ethylene. Sometimes, however, organometallic compounds are formed in which the cyclopropane ring is preserved intact. For example, Hart and Sandri[101] found that boiling finely divided lithium with cyclopropyl chloride in pentane solution yields cyclopropyllithium.

Reynolds *et al.*[102] obtained dicyclopropylmercury in 64% yield. They similarly obtained divinyl- and dipropenyl--mercury in 60 and 75% yield, respectively. In contrast to divinylmercury, dicyclopropylmercury does not decolorise potassium permangante solution.

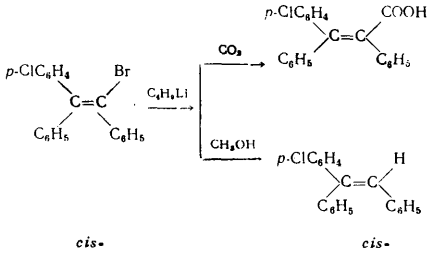
Shatenshtein *et al.*[103] studied the deuterium exchange between liquid deuterated ammonia and cyclopropane hydrocarbons in the presence of potassium amide. In this experiment the cyclopropane compounds act as electrophilic reagents, while most of the other work was concerned with their nucleophilic reactivity with electrophilic reagents (halogens, acids, etc.). The unsaturated character of the cyclopropane ring is manifested in a higher rate of hydrogen exchange as compared with saturated hydrocarbons.

It may be noted that in certain cases the behaviour of cyclopropane differs from that of alkenes. Hammond and Todd[104] found that in contrast to their olefinic analogues, some cyclopropane derivatives, including cyclopropyl cyanide and cyclopropyl methyl ketone did not react with various free radicals. Phenylcyclopropane completely resists polymerisation in the presence of benzoyl peroxide. Alkenes are known to undergo radical-initiated polymerisation with great ease.

Walborsky and Hornyak[105,106] compared certain properties of the cyclopropyl carbanion with those of the carbanions formed at trigonal carbon atoms (alkenyl anions).

According to Curtin and Harris[107], *cis*- and *trans*-1--bromo-2-*p*-chlorophenyl-1,2-diphenylethylenes on treat-

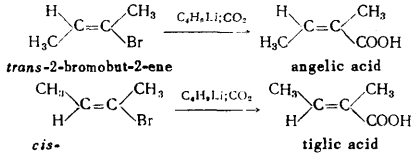
ment with n-butyllithium at -20° and subsequent carboxylation (or reaction with methanol) yield the corresponding *cis*- and *trans*-derivatives, respectively:



cis- *cis*-

All three reactions investigated, *i.e.* substitution of halogen by lithium, carboxylation, and substitution of lithium by hydrogen, are stereospecific. It was thus shown that the intermediate vinyllithium derivative preserves its configuration at -20°.

Somewhat later Dreiding and Pratt [108] confirmed this in another case:

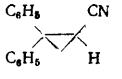


trans-2-bromobut-2-ene angelic acid

cis- tiglic acid

It was hereby shown that the alkenyl anion is capable of keeping its steric configuration.

Walborsky's experiments with an optically active nitrile showed that in this respect the analogy between the three-membered ring and the double bond breaks down:



since the cyclopropyl carbanion is unable to preserve its steric configuration§. On treatment with bisisopropylaminelithium at room temperature, the above cyano-compound is completely racemised. Alkenes and cyclopropanes also differ in their behaviour towards potassium permanganate. Cyclopropane does not react in the cold, while alkenes do so instantaneously. This is well illustrated by the reaction studied by Dem'yanov and Doyarenko [109]:



§ See, however, H.M.Walborsky, A.A.Youssef, and J.M.. Motes, J.Amer.Chem.Soc., 84, 2465 (1962).

Moreover, cyclopropane and its homologues do not react with dilute anhydrous bromine solution, and in contrast to alkenes, are not oxidised by air, and almost fail to react with ozone.

IV. CONJUGATION OF THE THREE-MEMBERED RING WITH UNSATURATED GROUPS

As already noted, the analogy between the three-membered ring and the double bond is especially clearly manifested in the capacity of cyclopropane for conjugation with unsaturated groups. This was first observed by Kishner [110], and later by Robinson [111]. Numerous publications are devoted to this interesting phenomenon.

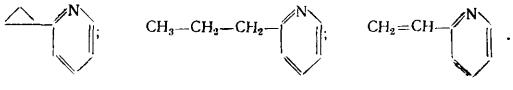
Conjugation of a three-membered ring has been studied in great detail by spectrographic methods, mainly ultra-violet absorption. Conjugation is measured by the bathochromic shift of the long-wavelength absorption band. For instance, the absorption maximum of ethylene in the ultra-violet region at 1750 Å shifts to 2170 Å in $CH_2=CH-CH=CH_2$, and to 2190 Å in $CH_2=CH-CO-CH_3$. A similar shift is observed in cyclopropane compounds conjugated with neighbouring unsaturated groups, although it is less pronounced than in dienes.

Many three-membered ring compounds of varied type were studied. Rogers [112] compared the spectra of simple cyclopropane derivatives with those of similar compounds in which the cyclopropane ring was substituted by an allcenyl or an allcyl group. The absorption band of compounds of type ▷-C=C occupies an intermediate position between the corresponding bands displayed by compounds of type R-C=C and C=C-C=C.

By spectrographic studies Roberts and Green [113], and later Hawthorne [114], established the presence of conjugation of the ring with the carbonyl group in the 2,4-dinitrophenylhydrazones of cyclopropane ketones.

Conjugation of the three-membered ring with the benzene nucleus in phenylcyclopropane was established from ultra-violet spectra by Carr and Burt [115] and later by Rogers [112]. Levina *et al.* [116] recently found that on going from phenylcyclopropane to tolyl- and anisyl-cyclopropane the absorption maximum is shifted bathochromically. They interpret this as increased conjugation of the cyclopropane ring with the aromatic nucleus containing nucleophilic substituents.

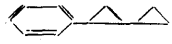
Mariella *et al.* [117] examined 2-cyclopropyl-, 2-n-propyl-, and 2-vinyl-pyridine by the same method and found the absorption maximum of the cyclopropane derivative to occupy an intermediate position between those of the conjugated and the unconjugated systems:



The work of Klotz [118] on steroid compounds containing a three-membered ring and on terpenes is noteworthy.

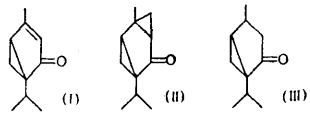
In their comparison of the ultra-violet spectra of chlorocyclopropane and cyclopropane, Eberlin and Pickett [119] observed a considerable bathochromic shift in the former, which they interpreted as indicating conjugation of the *p* orbital of chlorine with the three-membered ring.

The still unsolved problem of the possible transmission of conjugation by a three-membered ring has been discussed in a series of investigations which are discussed below. In 1951 Smith and Rogier[120] first synthesised 2-cyclopropyl-1-phenylcyclopropane:



Conjugation in 2-cyclopropyl-1-phenylcyclopropane was found to be no greater than it is in phenylcyclopropane, which may be interpreted by the absence from the former compound of a chain of conjugation involving both cyclopropyl rings. These authors therefore suggested that a cyclopropane ring is able to take part in a conjugation chain only as its terminal member, and is unable to transmit conjugation if located between two unsaturated groups.

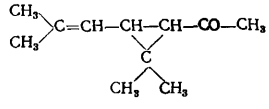
Eastman[121] made a spectroscopic study of the three compounds:



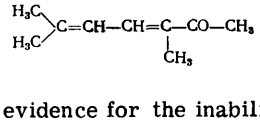
(I) (II) (III)

and observed that the spectra of compound (I) exhibited a pronounced conjugation effect, while those of compounds (II) and (III) did not differ essentially from one another. This was taken as evidence that in the tricyclic ketone (II) a chain of conjugation including both rings does not exist, while separately both rings are conjugated with the carbonyl group. However, such a chain of conjugation is found in compound (I).

Later Eastman and Freeman[122] synthesised and investigated the ketone of the following structure:

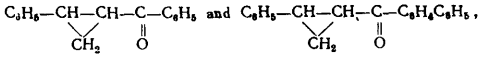


The combination of the double bond and the carbonyl group separated by a three-membered ring has very little similarity with the combination of two double bonds and a carbonyl group in the ketone of structure:



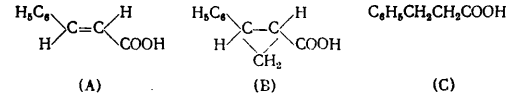
This was taken as evidence for the inability of the three-membered ring to transmit conjugation.

On the basis of their spectrographic studies of the ketones:



Mohrbacher and Cromwell[123] reached a different conclusion. A phenyl group in the β position of the cyclopropane ring shifts the absorption maximum in the ultra-violet bathochromically, which effect they ascribed to the ability of the three-membered ring to transmit the unsaturation of the phenyl group to the aroyl chromophore. Their point of view is shared by Cannon *et al.*[124]

Trachtenberg and Odian approached this problem using another, non-spectroscopic, method[125]. They studied the relative capacity of various substituents to affect the acidity of the carboxyl group in *trans*-cinnamic, *trans*-2-phenylcyclopropane-1-carboxylic, and β-phenylpropionic acids:



(A) (B) (C)

From the dissociation data of each acid series they calculated Hammett's constant (ρ) as: (A) 0.466; (B) 0.182; and (C) 0.204–0.212. Hammett's ρ constant for the cyclopropane series is very close to that for saturated analogues, so they concluded that the three-membered ring cannot transmit the conjugation effect, and that, like a saturated group, it isolates the carboxyl group from the influence of the phenyl ring.

This result, however, must not be taken as definite, since the comparison of Hammett's ρ constants for the alkaline hydrolysis of esters of the above acids led Fuchs and Blumfield[126] to an opposite conclusion. In their opinion the three-membered ring transmits conjugation, but much less so than the double bond.

Increase of the integral intensities of certain lines in Raman spectra is a far more sensitive criterion of the existence of conjugation than the bathochromic shift of the long-wavelength ultra-violet absorption bands. The absorption intensity for a double bond sharply increases (10–15 times) on conjugation with another double bond. This method is therefore well suited for the study of cyclopropane compounds, where conjugation is less pronounced. A systematic study of the conjugation of a three-membered ring by Raman spectra was carried out by Aleksanyan and his coworkers[127–130], and by Levina *et al.*[116,131,132]. From the spectrographic studies of systems such as vinylcyclopropane, isopropenylcyclopropane, and phenylcyclopropane, Aleksanyan and Sterin derived conclusive evidence of the existence of conjugation between a three-membered ring and a double bond or a benzene ring¶. The integral intensities of certain spectral lines of cyclopropane hydrocarbons and the corresponding model compounds are collected in Table 4. The intensities of the double bond lines of

TABLE 4.

Compound	Frequency, cm^{-1}		
	~1200	~1600	1640–1650
Pent-1-ene	—	—	340
Ethylcyclopropane	290	—	—
Vinylcyclopropane	430	—	660
2-Methylpent-1-ene	—	—	290
Isopropylcyclopropane	260	—	—
Isopropenylcyclopropane	410	—	620
Toluene	220	290	—
Isopropylbenzene	190	330	—
Phenylcyclopropane	800	1150	—

¶ This work was presented at the 10th All-Union Conference on Spectroscopy, 6th July 1956, and published in 1957 in the Report of the Conference. In 1957 there appeared in Vestnik Moskov. Gos. Univ., a paper by Levina *et al.*, in which, using the same method, they established the existence of conjugation between the three-membered and the benzene ring in arylcyclopropanes, particularly phenylcyclopropane.

vinyl- and isopropenyl-cyclopropane are nearly twice that of pent-1-ene and 2-methylpent-2-ene. The intensity of the lines in the ~1200 and 1600 cm^{-1} regions of phenylcyclopropane is even higher compared with that of alkylbenzenes of similar structure. The intensity of the lines in the ~1200 cm^{-1} region, which are due to the breathing frequency of the three-membered ring, are considerably higher in vinyl- and isopropenyl-cyclopropane than in alkylcyclopropanes, which emphasises the unsaturated character of the ring.

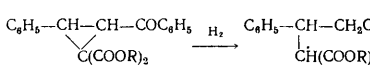
Aleksanyan and Sterin also studied the spectra of diphenyl- and phenylcyclopropyl-cyclopropanes and cyclopropane ketones. The reactivity of these compounds was studied simultaneously by Kazanskii, Lukina, and their coworkers, whose results will be discussed later in this review.

Levina, Treshchova, and their coworkers studied the Raman spectra of various arylcyclopropanes [116,131,132]. As mentioned earlier, this study included the ultra-violet spectra of these systems [116].

The presence of conjugation in a molecule can also be detected from other properties. Thus Rogers and Roberts [42] used dipole moments, and Kierstead *et al.* [133] and Kishner [110] the exaltation of molecular refraction. However, the validity of the latter method is controversial, since according to Jeffery and Vogel [134], and Slabey [135], exaltation of molecular refraction in the cyclopropane series may depend not only on conjugation, but also on the structure of the compound in question.

Kozina, Skuratov *et al.* [136] recently determined the heats of combustion of cyclopropane hydrocarbons, including phenylcyclopropane. This constant is also affected by conjugation.

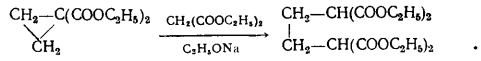
There is relatively little information in the literature on the reactivity of compounds in which the cyclopropane ring is adjacent to unsaturated groups. One of the first investigations in this field was carried out by Robinson [111], who interpreted several reactions in the terpene series by the conjugation of the three-membered ring with the double bond. In a number of examples Kohler and Conant [137] also stressed the analogy between α,β-unsaturated compounds and the cyclopropane derivatives containing a neighbouring C=O group. They carried out the reduction of a cyclopropane compound with nascent hydrogen which resulted in the opening of the three-membered ring:



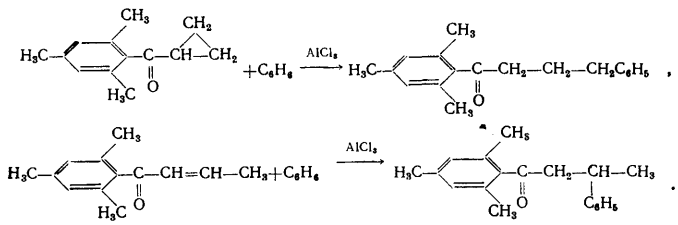
This reaction, one of the most specific for conjugated diene compounds may be taken as conclusive chemical evidence of the similarity between conjugation involving a three-membered ring and $\pi\pi$ conjugation. Nevertheless, attempts to add hydrogen in the 1,4-position of similar systems by reduction with metals in liquid ammonia were unsuccessful.

Greenfield *et al.* [138] observed that the action of sodium in liquid ammonia on vinylcyclopropane homologues resulted in the reduction of the double bond only. On reducing phenyl- and *p*-tolyl-cyclopropanes under similar conditions, Levina *et al.* [139] found that only the phenyl nucleus adds hydrogen. In both those cases the three-membered ring remained intact.

Bone and Perkin [140] showed that, like α,β-unsaturated esters, the diethyl ester of cyclopropane-1,1-dicarboxylic acid can add ethyl malonate, which contains a mobile hydrogen atom:

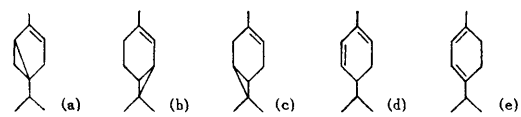


Fuson and Baumgartner [141] compared the behaviour of cyclopropyl mesityl ketone with that of mesityl propenyl ketone. Both ketones undergo condensation with aromatic hydrocarbons forming the corresponding butyromesitylenes:



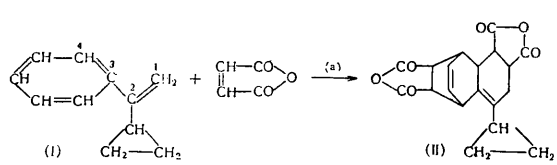
Cyclopropyl ketone does not, however, react with ethyl malonate or Grignard reagents, although α,β-unsaturated compounds do so.

In 1940 Gascoigne [142] reported that α-thujene, Δ^4-carene, and Δ^3-carene can take part in the Diels–Alder reaction with maleic anhydride or benzoquinone, forming adducts derived from α-phellandrene and α-terpinene:

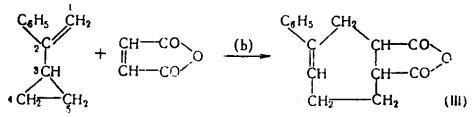


However, Trachtenberg and Odian [143] showed in 1958 that the above reaction is not a reaction of the Diels–Alder type involving systems of type (a), (b), and (c), since under the reaction conditions used (a), (b), and (c) undergo isomerisation to (d) and (e). Attempts to carry out the Diels–Alder reaction with vinylcyclopropane [144] or 1-phenyl-2-cyclopropylcyclopropane [120] were unsuccessful.

Sarel and Breuer [145] recently showed that vinylcyclopropane activated by a phenyl group is in fact an active conjugated system capable of taking part in the Diels–Alder reaction. For instance, on boiling for a long time with maleic anhydride in anhydrous benzene α-cyclopropylstyrene (I) reacts in two ways. The first yields 12% of the bis-adduct (II), in which the cyclopropane ring remains intact but the exocyclic double bond behaves as if conjugated with the aromatic nucleus. Addition takes place in the 1,4-position:

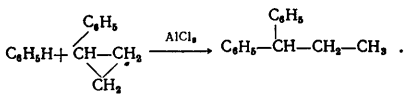


Another reaction simultaneously yields 40% of the adduct (III):

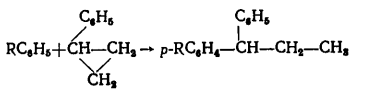


In the latter case the addition takes place in the 1,5-position and involves the exocyclic double bond and the cyclopropane ring, while the phenyl group remains intact.

Levina, Shabarov, and Shanazarova[146] studied the reaction of phenylcyclopropanes with benzene in the presence of aluminium chloride. Nenitzescu and coworkers[147] and Tsukervanik and Gar'kovets[148] had shown earlier that under those conditions styrene yields 1,1-diphenylethane. In this case also the double bond and the three-membered ring behave very similarly. Phenylcyclopropane yields 52% 1,1-diphenylpropane:



The yield of 1,1-diarylpropane is increased in the case of toluene (61.5%) and anisole (72.5%):



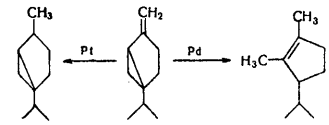
where R = CH_3; CH_3O. Alkylation proceeds only in the *para*-position of toluene and anisole, owing to the greater reactivity of the hydrogen atoms in that position.

Alkylation of benzene by *p*-tolyl- and *p*-anisylcyclopropane does not proceed as readily as that of phenylcyclopropane, and is accompanied by much polymerisation.

Levina and her coworkers[149] studied the reactivity of phenylcyclopropane in acylation by acetic anhydride in the presence of phosphoric acid and compared it with that of non-conjugated hydrocarbons of the cyclopropane series. Under the conditions employed, phenylcyclopropane underwent isomerisation, while the unsaturated hydrocarbons were acetylated.

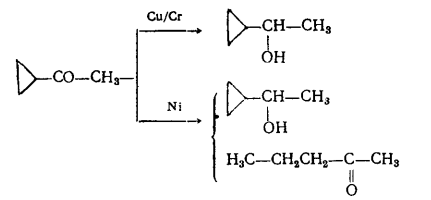
In their study of deuterium exchange in cyclopropane hydrocarbons in which the three-membered ring is conjugated with a multiple bond, Shatenshtein *et al.*[103] found that these systems are more reactive than alkylcyclopropanes in exchange reactions of this type.

The similarity between the behaviour of cyclopropane hydrocarbons containing unsaturated groups and that of conjugated systems is also observed in catalytic reductions. Richter *et al.*[150] found that the reduction of sabinene† by platinum black in ether solution at room temperature yields thujane, while reduction under the same conditions with palladium black yields an unsaturated hydrocarbon of the cyclopentane series. The authors think that in the latter case hydrogen is added on in the 1,4-position of the conjugated system ▷—C=C:



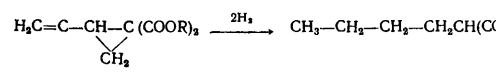
Later Short and Read[151] obtained the same results on hydrogenating sabinol with Adams catalyst.

In the hydrogenation of vinylcyclopropane and isopropenylcyclopropane over Raney nickel, Boord and his colleagues[144,152] discovered that besides alkylcyclopropanes the reaction product also contained alkanes. They think that this may be the result of addition of hydrogen in the 1,4-position of the starting hydrocarbons, assuming conjugation between the ring and the double bond. Hydrogenation of cyclopropyl methyl ketone led Slabey and Wise[153] to the same conclusion. They observe that, depending on the catalyst, hydrogen is added either entirely to the double bond of the carbonyl group (copper–chromium catalyst), or simultaneously to the carbonyl group and the three-membered ring (Raney nickel):



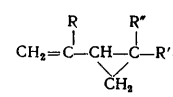
The same authors[154] found that hydrogenation of 2-cyclopropylalk-1-enes in the presence of copper–chromium catalyst yields the corresponding cyclopropylalkanes. Hydrogenated under the same conditions, 2-cyclopropylalk-2-enes gave, however, only small amounts of alkanes. The authors think that here also hydrogen is added in the 1,4-position.

The work of Kierstead *et al.*[133] is worthy of note. They found that under identical conditions of hydrogenation conjugated cyclopropane rings undergo opening, while non-conjugated ones do not. Unfortunately, their results are not very clear, since they used a rather complex starting compound:



where the three-membered ring is one of several unsaturated groups.

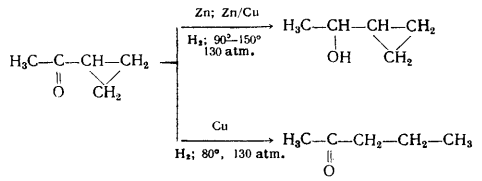
Nickl[155] succeeded in opening the three-membered ring of compounds of type



where R = CH_3; R′ and R″ = $COOC_2H_5$; or R = CH_3; R′ = CN; and R″ = $COOC_2H_5$, by hydrogenation under similar conditions. The two last groups of authors assumed that the first stage of hydrogenation consists of the addition of hydrogen in the 1,4-position of the conjugated system formed by the three-membered ring and the double bond.

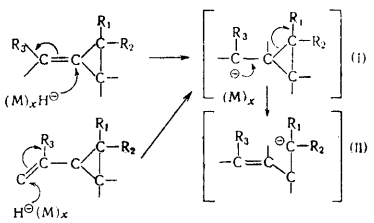
† I.U.P.A.C. name for compound shown is thuj-4(10)-ene (Ed. of Translation).

Freidlin *et al.*[156] studied the hydrogenation of cyclopropyl methyl ketone in the presence of Zn, Zn/Cu, and Cu catalysts and found that depending on the catalyst the reaction could proceed along different pathways:



Freidlin *et al.*[157] had shown earlier that during the hydrogenation of α,β-unsaturated ketones in the presence of zinc or zinc–copper catalyst, hydrogen is added to the carbonyl group, while in the presence of copper the double bond is hydrogenated first. The behaviour of cyclopropyl methyl ketone in this reaction is therefore very similar to that of α,β-unsaturated ketones.

In 1959 Ullman[158] expressed a different view of the hydrogenation mechanism for alkenylcyclopropanes. On the basis of the existing information that certain alkylidenecyclopropanes[159,160], like alkenylcyclopropanes, may undergo ring opening during hydrogenation under mild conditions, he suggested that the hydrogenation of both types of compounds proceeds *via* a common intermediate. Hydrogenation is preceded by the chemisorption of the organic molecule by the catalyst, which is followed by the attack of the hydride ion at the catalyst on the double bonds of vinyl- or alkylidene-cyclopropane. The result is the formation of the carbanion–metal complex (I). The carbanion may subsequently ring open to yield (II), or add a proton from the catalyst (or solvent) to form the "normal" 1,2-addition product:



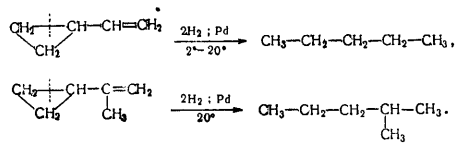
Protonisation of the decomposition product (II), and the concomitant saturation of the double bond must yield acyclic compounds. Taking as evidence his own results on the hydrogenation of certain alkylidenecyclopropanes, and published data on the hydrogenation of alkenylcyclopropanes, the author concluded that identical substituents had the same effect on the reaction course of both types of compounds, and thus confirmed his hypothesis on the mechanism of hydrogenation of alkenyl- and alkylidene-cyclopropanes. Unfortunately the author's own experiments were conducted under a different set of conditions and in the presence of various catalysts, so that they cannot be taken as reliable evidence of the effect of substituents. Ullman's hypothesis concerning the hydrogenation mechanism thus still remains to be proved.

As noted earlier, the catalytic hydrogenation and isomerisation of cyclopropane hydrocarbons has been long investigated by Kazanskii, Lukina, and their coworkers.

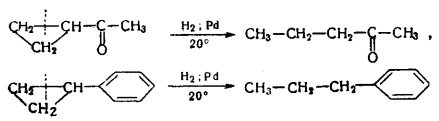
Since they used simple compounds and strictly standard reaction conditions they were able to compare the behaviour of various compounds. They observed that the principles underlying the behaviour of a great many alkylcyclopropanes do not hold for compounds in which the three-membered ring is adjacent to an unsaturated group. The reactivity of these systems is completely different, and can only be interpreted in terms of a unique type of conjugation.

The enhanced reactivity of such systems in catalytic reactions might not be sufficiently conclusive of conjugation had these investigations not been supported by studies of Raman spectra[127-130], by studies of reactivity and of deuterium exchange with potassium amide in liquid ammonia[103], and by the determination of heats of combustion[136]. The results of all these investigations accord well with the data on reactivity in catalytic hydrogenation.

In the presence of palladium black and hydrogen at room temperature, conditions which leave saturated cyclopropanes unaffected, conjugated cyclopropanes readily undergo hydrogenation and concomitant ring opening at the bond adjacent to the substituent. Alkenylcyclopropanes (vinyl-[161] and isopropenyl-cyclopropane[58]) react with two moles of hydrogen forming the corresponding alkanes:



Cyclopropyl methyl ketone[162] and phenylcyclopropane[163] react with one mole of hydrogen forming 2-butanone and n-propylbenzene, respectively.



Thus, on hydrogenation in the presence of palladium black, conjugated cyclopropane hydrocarbons and ketones show high reactivity, which is manifested in the readiness of the three-membered ring to open with the addition of hydrogen under conditions where a non-conjugated ring stays intact.

Palladium is a specific catalyst for this reaction. In the presence of other metals hydrogenation of conjugated cyclopropane compounds is very slow and non-specific. For instance, in the presence of platinum black, phenylcyclopropane[163] undergoes hydrogenation at one-ninetieth the rate in the presence of palladium, and the composition of the reaction mixture obtained shows that besides the cyclopropane ring, the benzene nucleus has also been hydrogenated.

Of special interest in these studies was the hydrogenation of diphenylcyclopropanes[164]. Here conjugation is only possible if the axes of the π clouds in the ring and the substituent are parallel or nearly so, that is, conjugation depends on the mutual orientation of the benzene and cyclopropane rings[128,163], as shown in Fig. 17.

Owing to steric effects, in disubstituted cyclopropane hydrocarbons the mutual orientation of these rings may assume different forms. Simple calculations show that not all conformations are possible in the *cis*-isomer because of the vicinity of the hydrogen atoms of different benzene rings (Fig. 18). In the *trans*-isomer, all conformations are possible since these rings are separated (Fig. 19). As a result, one of the substituents, or to a less extent both,

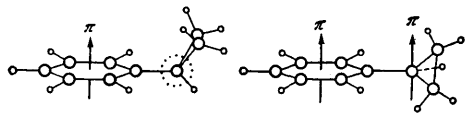


Fig.17.

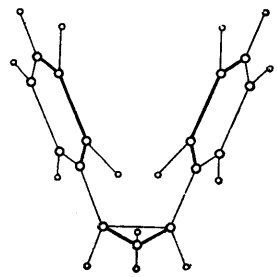


Fig.18.

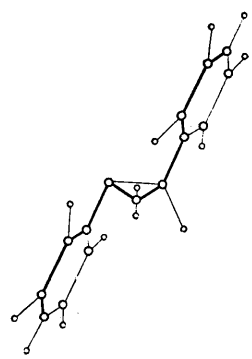
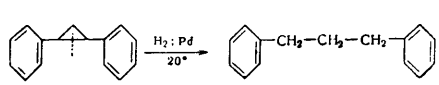


Fig.19.

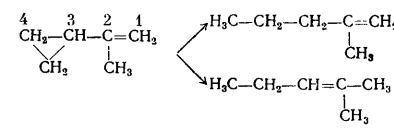
can be prevented from taking up a position suitable for conjugation. On these considerations it was possible to predict that conjugation could not take place in 1,1-diphenylcyclopropane, since the only possible spatial arrangement of the two phenyl groups is the one where the axes of their π clouds are not parallel with the plane of the three-membered ring.

All these considerations were confirmed by spectrographic studies [128,129] and later by catalytic hydrogenation [161]. In the latter reaction, 1,1-diphenylcyclopropane behaved as a non-conjugated hydrocarbon and did not combine with hydrogen, whereas 1,2-diphenylcyclopropane was hydrogenated:



The hydrogenation of *trans*-1,2-diphenylcyclopropane is considerably faster than that of the *cis*-isomer, and the latter is slower than the hydrogenation of phenylcyclopropane. This indicates that in the *cis*-isomer the optimum conditions for conjugation are disturbed for both phenyl rings. The reactivity of diphenylcyclopropanes therefore depends on the position of substituents in space, which accords well with the theoretical representations of the structure of a three-membered ring, which require the π electron cloud of this ring to be in the ring plane.

To explain the mechanism of hydrogenation of conjugated cyclopropane compounds in the presence of palladium black, partial hydrogenation of isopropenylcyclopropane was carried out in the presence of less than stoichiometrical amounts of hydrogen. In addition to unreacted isopropenylcyclopropane and 2-methylpentane, the reaction products also contained 2-methylpent-1-ene and 2-methylpent-2-ene.



2-Methylpent-1-ene may be formed by the addition of hydrogen in the 3,4-position, and 2-methylpent-2-ene as a product of 1,4 addition. However, it was established in a separate experiment that in the presence of palladium both hexenes are interconvertible, and form an equilibrium mixture. Each may therefore be considered as a secondary reaction product formed by the shift of the double bond. Nevertheless, experiments on incomplete hydrogenation showed that the three-membered ring undergoes hydrogenation first, and not the double bond in the substituent, otherwise the reaction product would contain isopropylcyclopropane. This indicates the special lability of a three-membered ring conjugated with an unsaturated group, as under the conditions employed in these experiments unconjugated three-membered rings resist hydrogenation, and double bonds are readily hydrogenated.

To conclude, the conjugation effect of the three-membered ring with unsaturated substituents during hydrogenation in the presence of palladium is manifested in the fact that the C–C bonds of cyclopropane are considerably weaker and affect the ring stability.

It was noted earlier [68-70] that the opening of the three-membered ring at the bond between carbon atoms carrying the largest and the smallest number of hydrogen atoms is typical of hydrogenation. However, it was not possible to study isomerisation in the presence of palladium, since in the absence of hydrogen, palladium caused no change in compounds under investigation, while in the presence of even small amounts of hydrogen it caused hydrogenation. Therefore, kieselguhr was used to study conjugated compounds under isomerisation conditions. A new interesting phenomenon was observed; in the presence of kieselguhr at 120° vinyl- [165] and isopropenyl-cyclopropane [166] are rapidly polymerised, *i.e.* they undergo a reaction most characteristic for conjugated systems. In addition to polymer, the catalysate also contains non-conjugated and conjugated diene hydrocarbons. In fact, under identical conditions the transformations of a conjugated hydrocarbon (isomerisation and polymerisation) are considerably more rapid than the transformations of the corresponding alkylcyclopropane (isomerisation).

Thus, this reaction also shows that the presence of conjugation considerably enhances the reactivity of a three-membered ring by lowering its stability.

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It is evident from this review of published information that the three-membered ring undoubtedly possesses unsaturated character, similar to that of the double bond. The unsaturation, however, is less pronounced in the cyclopropane series than in alkenes, as is brought out by the fact that the majority of reactions typical of alkenes are less marked in the cyclopropane series.

Investigations of systems in which the three-membered ring is conjugated with neighbouring unsaturated groups now being carried out by a great many methods (absorption and Raman spectra, dipole moments, heats of combustion, reactivity), show conclusively the existence of a similarity between these and conjugated systems. This is the most telling evidence in favour of the similarity of the three-membered ring and the double bond.

The experimental data discussed above are in good agreement with theoretical representations of the structure of a three-membered ring and give support to the basic ideas in the hypotheses of Walsh and Coulson and Moffitt.

It follows from the above considerations of their electron structure and properties that cyclopropane and its derivatives cannot be classified as cycloalkanes, a term used for alicyclic hydrocarbons. In fact cyclopropanes can only formally be classified with other polymethylene compounds (including cyclobutanes) in which the small distortions of the valence angles in the ring cause considerably less important changes in the hybridisation at the carbon atoms.

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ORGANIC COMPOUNDS OF BERYLLIUM, CALCIUM, STRONTIUM, AND BARIUM

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INTRODUCTION

The immense part played by magnesium compounds in modern organic chemistry is well known. The number of papers on methods of obtaining organomagnesium compounds, their structure, properties, and especially their use in organic synthesis is continually increasing and has reached many thousands[1]. Such intensive development of the chemistry of these compounds is explained by their extraordinarily high reactivity, which enables numerous derivatives of the most varied classes of compounds to be readily obtained.

In contrast to magnesium, the remaining elements of its subgroup received little attention, and it is only recently that the chemistry of the organic compounds of beryllium, calcium, barium, and strontium has begun to be developed. It therefore seems useful to make a short survey of the present position in this field, especially as its literature is scattered among various journals, which are often not readily available. The review by Jones and Gilman[2] considers very briefly only methods for obtaining these organometallic compounds, and the review published by Novoselova *et al.*[3] in 1958 deals only with organic compounds of beryllium.

The present review examines only compounds containing a carbon–metal bond. Thus it is not concerned with salts of organic acids, metal alkoxides, or similar compounds, nor with many complex compounds.

Since there are only a small number of publications we divide the review according to the metals. Each section includes methods of preparation, physical and chemical properties, and also (where information is available) the fields of application of the organometallic compounds.