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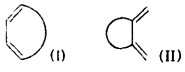
1, 2-DIMETHYLENECYCLOALKANES

Yu. A. Titov

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1. INTRODUCTION

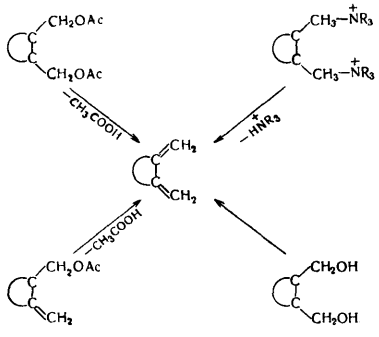
Conjugated dienes with double bonds fixed in a cisoid position are of great importance in the study of the properties of diene systems. Such a cisoid configuration occurs in cyclic dienes of type (I) and (II).



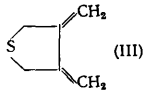
Dienes of type (I), for instance cyclopentadiene, have been known a long time and thoroughly investigated. Compounds of type (II), 1, 2-dimethylenecycloalkanes, whose conjugated systems consist of semicyclic double bonds, have received much attention lately. More than fifty dienes of type (II) which are derived from saturated or unsaturated polymethylene rings, or aromatic (*e.g.* acenaphthene) and heterocyclic (*e.g.* dioxane) systems are already known.

2. SYNTHESIS

The development of efficient methods for the preparation of 1, 2-dimethylenecycloalkanes presents difficulties owing to the readiness of these compounds to polymerise, oxidise, and isomerise. Only recently have the experimental obstacles been overcome, and most publications on the synthesis of this group of compounds have appeared in the last 5 to 7 years. The two basic methods available at present for the preparation of 1, 2-dimethylenecycloalkanes are the pyrolysis of 1, 2-bis(acetoxymethyl)cycloalkanes [1-21] and the Hofmann elimination of 1, 2-bis(dimethylaminomethyl)cycloalkanes [18,22-30]. For the preparation of certain particular compounds several other methods are also available – cyclopolymerisation of allenes, dehydration, etc. These methods can be used for the preparation of dienes containing 4-,[22-24] 5-,[3,18,25] and 6-membered [1,5-9,21,26] rings, and condensed [14,15] and bridged rings [11-13,18,27]. It has been reported that the products of pyrolysis of 1, 2-bis-(acetoxymethyl)cyclopropane contain 1, 2-dimethylenecyclopropane [31], which could not, however, be obtained pure.

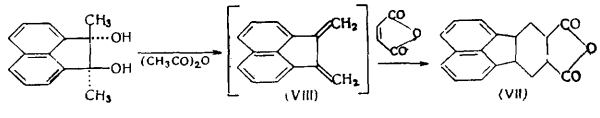


3, 4-Dimethylenethiophane(III) could not, however, be obtained by these methods [32,33].

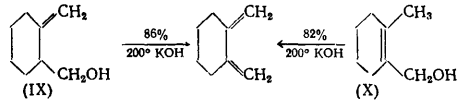


Some cases have been reported where different compounds were obtained instead of the expected 1, 2-dimethylenecyclohexanes [22,23,31-38].

A comparison of the two basic methods for the preparation of 1, 2-dimethylenecycloalkanes shows that the pyrolysis of acetates produces somewhat better yields, while the Hofmann elimination of diamines gives products of higher purity. The hydration of 1, 2-bis(hydroxymethyl)cycloalkanes over acid catalysts yields furans simultaneously, and is unsuitable for the synthesis of the corresponding dienes [39-40]. Nevertheless, on dehydration with acetic anhydride in the presence of maleic anhydride, *trans*-1, 2--dimethylacenaphthene-1, 2-diol produces good yields of the adduct (VII), corresponding to 1, 2-dimethyleneacenaphthene(VIII).[41]

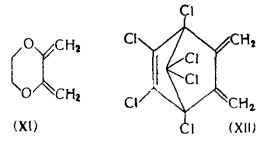


A paper has appeared recently [42] on the synthesis of 1, 2-dimethylenecyclohexane from alcohols (IX) and (X).

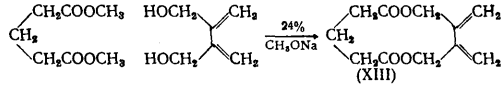


1,2-Dimethylene-3,3-dimethyl- and 1,2-dimethylene-3,3,4--trimethyl-cyclohexanes were prepared similarly [42].

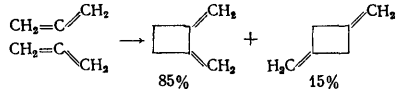
Dimethylenecycloalkanes (XI) [43] and (XII) [42] were prepared by dehydrohalogenation of the corresponding dihalides in the presence of alkali. The same method was used for the synthesis of 1, 2-dimethylenecyclohexane [45], but the authors did not give either the details of the preparation, or the yield of the diene.



The reaction of 2, 3-bis(hydroxymethyl)butadiene with the dimethyl ester of glutaric acid was used to synthesise a diene (XIII), which has an eleven-membered ring containing oxygen [46].

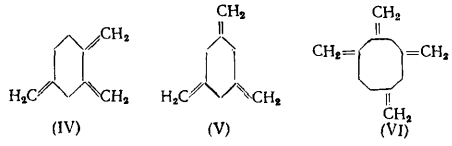


The thermal dimerisation of allene and its homologues yields 1, 2-dimethylenecycloalkanes with a four-membered ring [23,37,47-50].



The homologues of allene containing alkyl and aryl substituents [39,47,51,52] and also tetrafluoro- [53] and tetrachloro--allene [54] react in the same way.

Cyclopolymerisation of allene [55] in the presence of the catalyst $Ni(CO)_2[P(C_6H_5)_3]_2$ gave trimers and tetramers of allene with the following structures:



3. ULTRA-VIOLET AND INFRA-RED SPECTRA

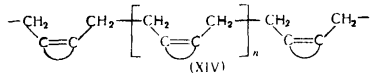
1, 2-Dimethylenecycloalkanes may be clearly divided according to their ultra-violet spectra into two groups: 1) dienes with a six-membered ring and 2) dienes with any other ring, including those containing bridges. Dienes of the first group have an absorption maximum at 213–221 mμ.[1,23,26,32,56,57], and those of the second group at 241–253 mμ [11-13,16,18,22,27,38,58]. The maximum calculated

for 1,2-dimethylenecycloalkanes from the Woodward rule[59] is at 237 mμ; thus, for neither group of dienes do the absorption maxima agree with the calculated value†. The bathochromic shift of the absorption maximum in dienes of the second group apparently occurs as a result of strain in their cyclic systems. 1,2-Dimethylenecycloalkanes of the first group (six-membered rings) show a hypsochromic shift in λ_{max} of approximately 20 mμ from the calculated value. This is most probably explained by non-coplanarity of the exocyclic double bonds in such systems[6,11,16,26,56]. This view is confirmed by the observation of exactly the same hypsochromic shift (~ 20 mμ) after the loss of coplanarity for cisoid dienes with a different configuration, *i.e.* where the ring is closed in the 1,4-position of the diene system (cycloheptadiene, λ_{max} 248 mμ, and cyclo-octadiene, λ_{max} 228 mμ[60]). The molecular extinction coefficient ϵ is less than 10 000 in both groups of 1,2-dimethylenecycloalkanes. Variations in the intensity of absorption are connected primarily with the purity of the diene. The value ϵ_{max} = = 10 000 is evidently characteristic of the cisoid conformation of the diene system (the transoid conformation is characterised by ϵ_{max} of the order of 20 000).

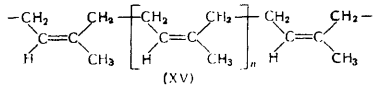
The infra-red spectra of 1,2-dimethylenecycloalkanes display frequencies characteristic of conjugated double bonds, methylene groups, etc.[6,10,41,18,22,33,34,44,58,61]. However, owing to the diversity of the observations and in some cases to the insufficient purity of the substance, no general conclusions can be drawn from them, except to note that they do not show the anomalies characteristic of the spectra of acyclic dienes.

4. POLYMERISATION

The development of the chemistry of 1,2-dimethylenecycloalkanes is primarily connected with the problem of stereospecific polymerisation. Polymerisation of these dienes is important as it is expected to be certain to give *cis*-1,4-polymers (XIV), that is complete structural analogues of natural rubber (XV), which should display some of its invaluable properties:



(XIV)

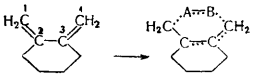


(XV)

The radical, ionic, and thermal polymerisation of 1,2-dimethylenecycloalkanes have so far been insufficiently studied.

As a rule, 1,2-dimethylenecycloalkanes polymerise more readily than the corresponding acyclic dienes. For instance, under the same conditions polymerisation of 1,2-dimethylenecyclobutane yields 96% polymer, whereas only 13% polymer is obtained from its open-chain analogue (2,3-dimethylbutadiene).[22] However, the ease of polymerisation depends essentially on the method used. Thus, 1,2-dimethylenecyclohexane polymerises well in various emulsion systems, or in the presence of BF_3 or $AlCl_3$ at -70°, but worse in the bulk in the presence of benzoyl peroxide, and not at all under Ziegler's conditions, *viz.* $TiCl_4$ + $Al(iso\text{-}C_4H_9)_3$, 50°, 24 h.[26,45,62] On the other hand, 1,2-dimethylenedecalin does not polymerise at all under the influence of peroxides, but in the presence of BF_3 it yields 47% polymer[15].

The connection between the reactivity of 1,2-dimethylenecycloalkane monomers and their spatial configuration is of particular interest. Blomquist and his coworkers[25,26] compared the polymerisation of 1,2-dimethylenecycloalkanes containing various numbers of carbon atoms in the ring. It was shown that the diene with a six-membered ring polymerises considerably more slowly than its analogues with four- and five-membered rings. This difference was related to the dissimilar spatial configurations of the exocyclic double bonds. In dienes with four- and five-membered rings the double bonds are rigidly fixed in the planar cisoid configuration, while in 1,2-dimethylenecyclohexane, if the cyclohexane ring has the thermodynamically favoured chair conformation[63], the double-bond system is not planar (the deviation from coplanarity can reach 60°). It was assumed that this was the reason for the reduced reactivity of the monomer to 1,4-addition. The transition state in 1,4-addition requires the formation of a double bond in the 2–3 position, and consequently bending the system of carbon atoms 1,2,3,4 into a coplanar or nearly coplanar position.



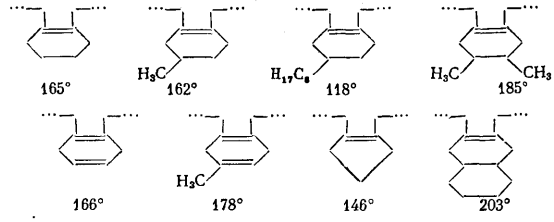
This is the reason for the greater energy required for the polymerisation of dienes with six-membered rings as compared with that needed for polymerisation of their four- and five-membered analogues where the diene system is coplanar[56]. It is impossible, at present, to tell whether this factor is completely responsible for the decreased reactivity of 1,2-dimethylenecyclohexane.

Another type of steric hindrance was observed in 3-methyl- and 3,6-dimethyl-1,2-dimethylenecyclohexane[7], which polymerise with difficulty, owing to the screening of the diene system by methyl groups; however, the copolymers of these dienes with 1,2-dimethylenecyclohexane were obtained relatively easily. The same type of steric hindrance was thought responsible for the failure of 1,2-dimethylenedecalin to polymerise with peroxide initiation[15].

As already mentioned, from their analogous structures the properties of poly-1,2-dimethylenecycloalkanes were expected to be similar to those of natural rubber. The first studies on this point, by Bailey and coworkers[56,62,64,65], gave completely unexpected results. Although infra-red spectra and X-ray analysis of the polymer of 1,2-dimethylenecyclohexane showed it to have similar structure to natural rubber, it did not possess rubber-like properties, and was found to be a solid crystalline compound with a sharp softening point (165°), soluble in benzene, decalin, and other organic solvents. Several similar polymers,

† It should be noted that the recently synthesised[43] 1,2-dimethylene-3,3-dimethylcyclohexane and 1,2-dimethylene-3,4,4-trimethylcyclohexane have absorption maxima close to the calculated value, at 233 and 230 mμ, respectively.

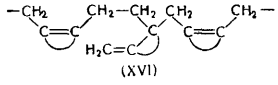
differing in degree of unsaturation, ring structure, molecular symmetry, softening point, etc. were obtained later:



Comparison of the softening points and solubilities of these polymers indicates that their properties are determined primarily by the general geometry of the molecule. Rubber-like polymers are obtained from the least symmetrical molecules. Ring substituents also play a part, although a minor one compared with the symmetry. Thus, changing from a methyl to an *n*-octyl substituent on the six-membered ring reduces the softening point of the resulting polymer by 44°.[56] The lack of elasticity in polymers of this type was accounted for by steric hindrance of the rings to internal rotation in the macromolecules‡.

The hydrogenation of poly-1,2-dimethylenecycloalkanes lowers their softening points. Thus hydrogenation of poly-1,2-dimethylenecyclohexane (softening point 165°) over a nickel-on-kieselguhr catalyst, in decalin solution, at 200° and 120 atm, gives a product which softens at 110°. The softening points of partially hydrogenated polymers lie between 110° and 165°.[67]

Some modification of Bailey's ideas resulted from the fact that the softening point of the polymer depends on the method of preparation[33]. For instance, on bulk polymerisation with SO_2, 1,2-dimethylenecyclobutane yields a crystalline polymer, softening point 170°,[25] while on emulsion polymerisation with $K_2S_2O_8$ [25,26] or bulk polymerisation with benzoyl peroxide[68] it gives elastic rubber-like polymers. It was also found that in most cases the polymers are not exact structural analogues of natural rubber, but contain a certain number of 1,2-links, the number apparently depending not only on the nature of the monomer, but also on the method of polymerisation. The structure of such polymers can be represented by formula (XVI):



(XVI)

A study has been made recently of the ability of 1,2-dimethylenecycloalkanes to polymerise under various conditions, and their softening points and the relative amounts of 1,4- and 1,2-links in the polymer chain have been determined. The results are collected in the Table. This study did not include estimation of the mechanical properties of the polymers.

Copolymerisation of 1,2-dimethylenecycloalkanes with other monomers, besides that of 1,2-dimethylenecyclohexane with its methylated homologues[7] already mentioned, has been described in patents. 1,2-Dimethylenecyclohexane has been copolymerised (in emulsion or with BF_3) with butadiene, chloroprene, styrene, various derivatives

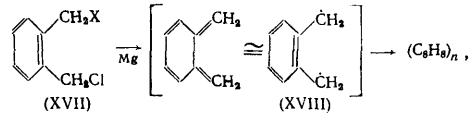
TABLE. Polymerisation of 1,2-dimethylenecycloalkanes.

Monomer	Method of polymerisation	Monomer conversion, %	Mol. weight of polymer*	*cis*-1,4-links, %		Polymer properties	Ref.
				from IR spectra	from $C_6H_5CO_3H$ oxidation		
1,2-Dimethylenecyclobutane	emulsion $K_2S_2O_8$			80	80	rubber-like	22,23
1,2-Dimethylenecyclopentane	emulsion $K_2S_2O_8$, 50°	100		100	94	rubber-like	18,25,26
1,2-Dimethylene-3-methylcyclopentane	emulsion $K_2S_2O_8$, 50°, 24 h	100		100	72	rubber-like	18,25,26
1,2-Dimethylenecyclohexane	emulsion or BF_3 at −70°	55	100 000	100		softg. pt. 164.5°–165°	62
1,2-Dimethylenecyclohexane	emulsion $K_2S_2O_8$, 50°, 60 h	100		100		softg. pt. 148°–152°	26
1,2-Dimethylene-4-neopentylcyclohexane	emulsion				66	rubber-like	57
1,2-Dimethylene-4-octylcyclohexane	emulsion with peroxide		30 000			softg. pt. 109°–118°	66
1,2-Dimethylenebicyclo[2,2,1]-heptane	emulsion with peroxide		50 000	70		softg. pt. 90°	12
1,2-Dimethylenebicyclo[2,2,2]-octane	emulsion with peroxide		40 000	85		softg. pt. 190°	12
1,2-Dimethylenedecalin	BF_3 at −70°	57				softg. pt. 102°–112°	15

* Molecular weight of polymer estimated from viscosity data.

of acrylic and methacrylic acids, vinyl chloride and acetate, and methoxyethylene. The resulting oily or rubber-like products were suggested for use as plasticisers or siccative oils[45]. 1,2,4-Trimethylenecyclohexane was reported[67] to form a viscous rubber-like copolymer with butadiene under the action of lithium in cyclohexane at −70°.

A series of papers deals with the preparation of the solid poly-*o*-xylylene, the polymer of 1,2-dimethylenecyclohexa-3,5-diene [*o*-quinodimethane (XVIII)]. According to molecular orbital calculations[61,68], compound (XVIII) must have a biradical character (the free-valency index of the carbon atoms in the methylene groups is 0.96), and consequently should polymerise readily. In fact, efforts to synthesise *o*-quinodimethane by pyrolysis of the corresponding diacetate[69] or by the action of magnesium on compound (XVII) (where X = Cl, OCH_3, OC_6H_5) [70] resulted only in poly-*o*-xylylene:



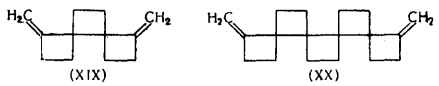
(XVII) (XVIII)

Poly-*o*-xylylene also results from pyrolysis of *o*-xylene[69,71]. However, mass-spectrometer data indicate that at a high temperature (825°–1000°) and low pressure (10^{-3} mm) *o*-quinodimethane monomer is formed from *o*-xylene[72].

1,2-Dimethylenecycloalkanes are distinguished by the ease of their thermal polymerisation. 1,2-Dimethylene-3,6-dioxane, after 24 h at 25°, yields quantitatively a white vitreous thermopolymer, m.p. 240°. There are reports of the polymerisation, on standing or heating, of 1,2-dimethyleneacenaphthene[73,74], 1,2-dimethylenecyclobutane[47,75], and 1,2-dimethylene-3,3,4,4-tetramethylcyclobutane[47], all giving solid thermopolymers without

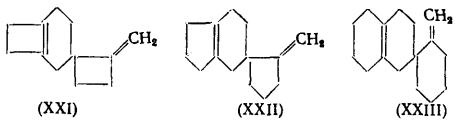
‡ In contrast to the polymers mentioned above, the chlorinated diene polymer (XII) obtained in the presence of peroxides, softens above 180°, and does not have a crystalline structure[44].

elastic properties. Only the structure of the 1, 2-dimethylenecyclobutane polymer, obtained at 200° (1.25 h) was investigated. It softens at 81° and melts at 162°–165°. Its degree of unsaturation, determined by bromination, corresponds to an average degree of polymerisation of 11.5, and its structure is that of the usual 1, 4-addition type (XIV).[47,75] Lebedev[47] also isolated thermopolymers formulated with a spiro structure (XIX) and (XX); this structure has, however, been questioned recently[53].



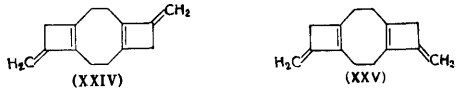
(XIX) (XX)

Thermal polymerisation of 1, 2-dimethylenecycloalkanes is almost always accompanied by, and sometimes results only in the formation of cyclic dimers. Lebedev[47], the first to study this phenomenon, isolated about 5% 1, 2--dimethylenecyclobutane dimer, to which he ascribed the structure (XXI), by heating allene in a sealed tube. Similar formulae were adopted for the dimers of 1, 2-dimethylenecyclopentane (XXII) [18] and 1, 2-dimethylenecyclohexane (XXIII) [76] on the basis of their infra-red spectra (and oxidation by $KMnO_4$).



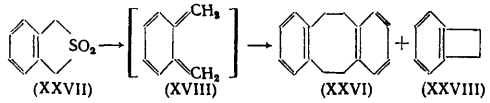
(XXI) (XXII) (XXIII)

Trimethylenecyclobutane dimerises at room temperature to a compound which, from its infra-red and ultra-violet spectra, is ascribed the eight-membered ring structure (XXIV) or (XXV) [37].



(XXIV) (XXV)

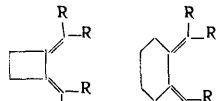
The eight-membered ring dimer, 1, 2: 5, 6-dibenzocyclo--octa-1, 5-diene (XXVI), is also formed from 1, 2-dimethylenecyclohexa-3, 5-diene (XVIII), which is an intermediate product in the pyrolysis of the sulphone (XXVII). The tetraene (XVIII) undergoes either intermolecular cyclisation, giving the dimer (XXVI), or intramolecular cyclisation forming benzocyclobutane (XXVIII). In the liquid phase pyrolysis of the sulphone (dissolved in diethyl phthalate at 300°) the product (XXIV) predominates, while the reaction in the vapour phase at 460°–770° yields mainly (XXVIII).[77] Other compounds containing an *ortho*-quinonoid system of double bonds cyclise in like manner[78,79].



(XXVII) (XVIII) (XXVI) (XXVIII)

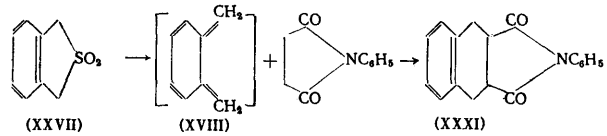
5. DIENE SYNTHESES

1, 2-Dimethylenecycloalkanes react readily not only with highly reactive dienophiles such as maleicanhydride and tetracyanoethylene[80], but also with ethylene[81]. The extra reactivity is expected because the transition state for diene synthesis requires the *cis*-configuration of the diene[82]. The reactivity of the dienes studied is not greatly affected by the ring size or the presence of alkyl substituents, although the introduction of a double bond or a carbon bridge into the ring considerably lowers the yield of adducts. Certain 1, 2-dimethylenecycloalkanes, for example the chlorinated diene (XII), are completely inactive in the diene synthesis, and this is explained by their diene system not being coplanar owing to the chlorine atoms in the bridge[44]. The ability to take part in diene condensation is also lost when the double bonds are screened by substituents, *e.g.* compounds of type (XXIX) and (XXX) (R = CH_3 or C_6H_5) do not react with maleic anhydride[39,83–85].



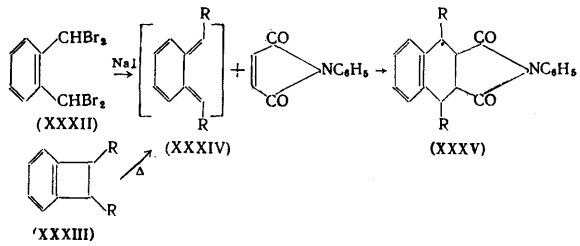
(XXIX) (XXX)

Many 1, 2-dimethylenecycloalkanes are very unstable in the free state, and condensations involving them must be carried out on the reaction mixture without their isolation. Examples are 1, 2-dimethyleneacenaphthene[41], 1, 2, 4-trimethylenecyclohexane[55], and the unisolatable *o*-quinodimethane (XVIII). Pyrolysis of the sulphone (XXVII) at 260° in the presence of *N*-phenylmaleic imide gives the adduct (XXXI) in 78% yield[77].



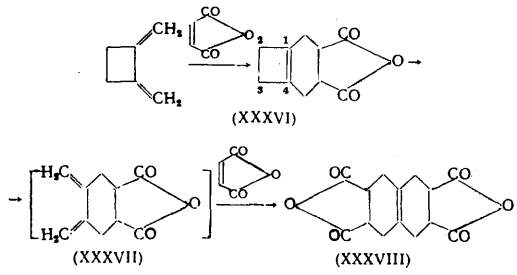
(XXVII) (XVIII) (XXXI)

Similarly, tetrabromo-*o*-xylene (XXXII) [86] and 3, 4-di-ido- or 3, 4-diphenyl-1, 2-benzocyclobutane (XXXIII) (R = I or C_6H_5),[87,88] yield as intermediate products the corresponding derivatives of *o*-quinodimethane (XXXIV), where R = Br, I or C_6H_5, which give the adducts (XXXV) with dienophiles. Unsubstituted 1, 2-benzocyclobutane does not react in this way[77].



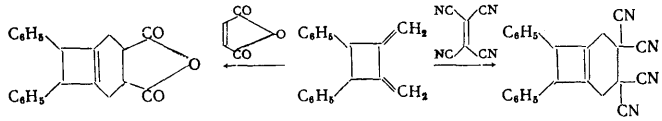
(XXXII) (XXXIV) (XXXV) (XXXIII)

A cyclobutene ring formed in the diene synthesis is unstable. For instance, in the condensation of 1, 2-dimethylenecyclobutane with maleic anhydride[22,48,49] at room temperature or in boiling benzene, the monoadduct (XXXVI) is formed, but heating at 150° ruptures the 2, 3-bond of the cyclobutene ring; the intermediate (XXXVII) then gives the diadduct (XXXVIII).



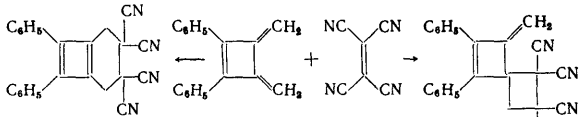
(XXXVI) (XXXVII) (XXXVIII)

Rupture of the cyclobutene ring in diene synthesis seems to be a general rule, and is the result of activation of the β--position by the presence of a double bond in the four--membered ring[89-92]. It is interesting that the reactions of 1, 2-dimethylene-3, 4-diphenylcyclobutane (XXXIX) with maleic anhydride and tetracyanoethylene are exceptions to this rule, yielding the normal monoadducts (XL) and (XLI), without rupture of the cyclobutene ring[28].



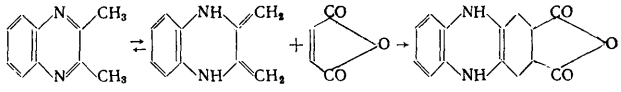
(XL) (XXXIX) (XLI)

The behaviour of the unsaturated hydrocarbon (XLII) is peculiar since with tetracyanoethylene it forms adduct (XLIV) instead of the substituted cyclobutadiene (XLIII). The spiro structure of (XLIV) was adopted on the basis of its infra-red spectrum[28,93]:



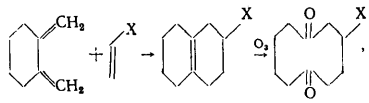
(XLIII) (XLII) (XLIV)

Dimethylene derivatives of heterocyclic compounds react with dienophiles according to the general scheme for diene synthesis[43]. For example, 2, 3-dimethylquinoxaline reacts in its tautomeric form (XLV) with dienophiles to give the normal adduct (XLVI)[94,95].



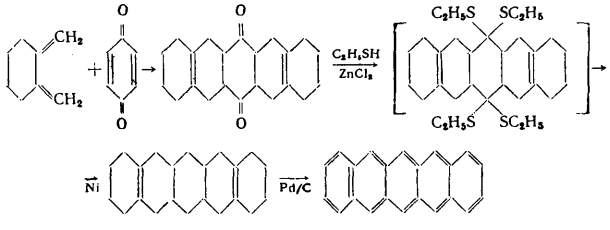
(XLV) (XLVI)

Adducts of 1, 2-dimethylenecycloalkanes with various dienophiles can be used for the synthesis of compounds otherwise difficult to obtain. For instance, ozonolysis of adducts of 1, 2-dimethylenecyclohexane gives cyclodecane derivatives in high yields[96]:

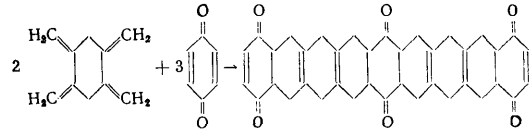


where X= $COOC_2H_5$, $COOCH_3$, NO_2.

Adducts of 1, 2-dimethylenecycloalkanes with quinones can be used to prepare linear fused aromatic hydrocarbons[5,97-100]. Pentacene, for example, has been synthesised in 30% yield as follows[98]:

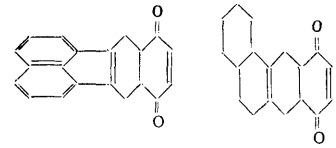


Condensation of two molecules of 1, 2, 5, 6-tetramethylenecyclohexane with three molecules of quinone gave adduct (XLVII), from which nonacene was obtained by the above method[21]:



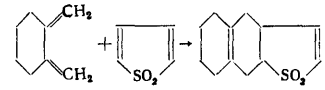
(XLVII)

Adducts of 1, 2-dimethyleneacenaphthene[41] and 1, 2-dimethylenedecalin[15] offer interesting possibilities for the synthesis of fused aromatic hydrocarbons. With quinone they give respectively adducts (XLVIII) (a derivative of 8, 9-benzofluoroanthene) and (XLIX) (derivative of 1, 2--benzanthracene).



(XLVIII) (XLIX)

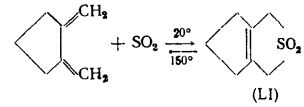
Finally, the reaction of 1, 2-dimethylenecycloalkanes with thiophene 1, 1-dioxide is used to prepare sulphur. heterocycles of type (L):[101]



(L)

6. OTHER CHEMICAL PROPERTIES

1, 2-Dimethylenecycloalkanes react with sulphur dioxide to form cyclic sulphones. With SO_2 1, 2-dimethylenecyclopentane gives (two days, 20°) 60% yield of the sulphone (LI), which decomposes at 145° – 150° into the starting compounds[18].



(LI)

1, 2-Dimethylene-4-neopentylcyclohexane also forms a sulphone[57], while 1, 2-dimethylenecyclobutane gives with SO_2 a sulphur-free polymer and not the expected sulphone[22].

Oxidation and ozonolysis of 1, 2-dimethylenecycloalkanes have been used in structure determination. The C – C bond lying between the methylene groups ruptures during oxidation to yield the corresponding diacids[22-25]. On ozonolysis, 1, 2-dimethylenecyclohexane[6] gave adipic acid in 75% yield, and 1, 2-dimethylenebicycloheptane[11] gave 17% *cis*-cyclopentane-1, 3-dicarboxylic acid. Dicarboxylic acids are also obtained by the oxidation of 1, 2-dimethylenecycloalkanes with $KMnO_4$ [47,53] or $Na_2Cr_2O_7$.[73] The methylene groups are not then oxidised to formaldehyde, as in ozonolysis, but to formic acid.

Dimethylenecycloalkenes isomerise readily to form aromatic compounds on heating for a short time with palladium deposited on charcoal. In the conversion of dimethylenecyclohexene to a benzene derivative about 30 kcal $mole^{-1}$ are liberated. 1, 2-Dimethylenecyclohex-4-ene isomerises

to *o*-xylene in 97% yield[102]; its homologues react likewise[4,10]. Isomerisation of 1,2-dimethylene-3,6-dimethylcyclohex-4--ene[10] yielded only 40% 1,2,3,4-tetramethylbenzene, however. This was accounted for by repulsion of the methyl and methylene groups, hindering the aromatisation. Heating 1,2-dimethylenecycloalkenes with hydrochloric acid also causes their conversion to aromatic hydrocarbons, but in considerably smaller yield than with palladium[2,4,102]. 1,2,4-Trimethylenecyclohexane isomerises to trimethylbenzene in good yield on boiling with chloroform in the presence of *p*-toluenesulphonic acid[55]. Aromatisation is not complete if this triene is treated with t-butyl potassium.

Other reactions of 1,2-dimethylenecycloalkanes have not been studied to the same extent. Hydrogenation or bromination of these dienes is known to proceed normally, *viz.* by the addition of two molecules of hydrogen or bromine to one molecule of diene[1,23,29,44]. The addition of one molecule of halogen (Cl_2 or Br_2) to the triene (XII) takes place at the 1 and 4 positions of the diene system[44], but hydrogen chloride reacts with 1,2-dimethylenebicycloheptane at the 1 and 2 positions[17].

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THE PRESENT STATE AND FUTURE DEVELOPMENT OF CO-ORDINATION CHEMISTRY

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I. IMPORTANCE OF APPLICATIONS OF CO-ORDINATION CHEMISTRY

The name "co-ordination chemistry" shows that this branch of chemistry was based on Werner's co-ordination theory, but considerable development has taken place from the theory put forward in 1893 to co-ordination chemistry as it stands today. About forty years ago, at the time of Werner's death, co-ordination theory dealt with material which was regarded as part of inorganic chemistry and included a group of compounds whose compositions could not be explained satisfactorily by classical valency theory.

The chemistry of complex compounds was regarded as an extremely specialised branch of chemistry and many organic and physical chemists considered it unnecessary to become familiar with it. Gradually, however, it became apparent that co-ordination theory was of great importance for the development of adjacent fields of science, and as a result, co-ordination chemistry ceased to be merely a branch of inorganic chemistry and became a field of interest to inorganic, organic, analytical, and physical chemists, biochemists, chemical crystallographers, and technologists in different fields. It first became clear that complex compounds were extremely important for developing analytical chemistry, and an important part was played by Chugaev, whose work on dioximes[1] laid the foundation for the systematic application of co-ordination complexes in qualitative and quantitative analysis. Dimethylglyoxime, dicyandiamidine[2], cupferron[3], and α-nitroso-β-naphthol, proposed for the determination of cobalt[4] as early as 1885, were the first successful examples of the use of organic reagents in chemical analysis.

It would be difficult now to list briefly the reagents proposed for qualitative detection or quantitative determination of individual elements. The methods of applying the reagents have also become extremely varied, and extend beyond their use for precipitation and colour reactions. Of particular importance is the use of complex-forming ligands in combination with extraction and ion-exchange methods. These processes are finding ever-increasing application for the separation and purification of lanthanides and actinides. Also we have the sequestering agents, which make it possible to bind complex-forming metals as very stable soluble complexes and so eliminate the catalytic influence of their ions on processes of technological or biochemical interest[5]. It is well known that the technology of the platinum group metals is entirely based on the use of complex compounds, and that the principal process for extracting gold from its ores (cyanide process) is also based on complex formation.

It has recently become clear that complex compounds are of considerable importance as catalysts or intermediate products in a variety of organic syntheses[6]. The change in the reactivity of organic ligands accompanying complex formation with a metal is particularly important. It is also important that the product formed by the organic molecules or ions with the complex-forming metal should be sufficiently labile to allow the process to occur again. Some examples of processes of practical importance where complexes act as catalysts are: (a) catalytic oxidation of