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Functionally Substituted Cyclopropanes

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Progress in the synthesis of functionally substituted cyclopropanes is surveyed together with certain of their properties as well as aspects of their structure and the transmission of electronic effects through the cyclopropane ring. A list of 225 references is included.

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I. INTRODUCTION

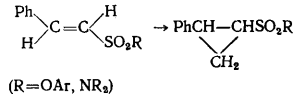
Functionally substituted cyclopropanes are of considerable interest. Firstly, they are fairly widely distributed in Nature. Examples are well known insecticides present in pyrethrum (*Chrysanthemum cinerariaefolium* Vis.), which are chrysanthemic esters and pyrethrolone or cinerolone ethers; and *cis*- and *trans*-isomers of 2-chloro-3-non-7'-ene-1',3',5'-triynylcyclopropylmethyl acetate have recently been detected[1] in *Centaurea ruthenica* Lam. The attractant of the American cockroach *Periplaneta americana* is also a cyclopropane derivative, for which the structure 2-isopropylidene-3,3-dimethylcyclopropyl propionate was suggested[2]. Furthermore, several cyclopropane derivatives, e.g. 2-(2,6,10,14-tetramethylpentadeca-1,5,9,13-tetraenyl)-3-(4,8,12-trimethyltrideca-3,7,11-trienyl)cyclopropylmethyl pyrophosphate (prephytoene pyrophosphate), are intermediates in the biosynthesis of steroids and carotenoids[3]. Several cyclopropane derivatives possess interesting physiological properties, like the above-mentioned derivatives of chrysanthemic acid, which have hitherto attracted the attention of chemists seeking new insecticides[4,5]. They exhibit not only insecticidal but also other types of activity. Thus several ketones have shown high anti-inflammatory activity[6].

The use of functionally substituted cyclopropanes as a convenient model for studying the ability of the cyclopropane ring to conjugate with the π-electrons of multiple bonds and examining the transmission of electronic effects through the ring has enabled a considerable approach to be made during recent years to solving this most complicated problem. Finally, several behavioural peculiarities of functional groups attached to a cyclopropane ring have been discovered recently.

The growing interest in functionally substituted cyclopropanes has led to the appearance of many publications on their synthesis, structure, and properties, but no systematic review of these results. The last survey of cyclopropane chemistry appeared in 1962 [7] and, of course, does not represent the present-day situation. The well known Houben—Weil work of reference[8] (1971) deals with methods for synthesising a cyclopropane ring irrespective of their possible use to obtain particular functional derivatives. We have therefore considered it useful to examine the most important papers on the synthesis, properties, and theoretical aspects of the chemistry of functionally substituted cyclopropanes which appeared between 1962 and 1973, referring to earlier work only in cases of extreme necessity.

II. SYNTHESIS OF FUNCTIONALLY SUBSTITUTED CYCLOPROPANES

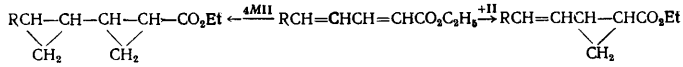
A most important advance in the synthesis of functionally substituted cyclopropanes during this period has been the practical introduction of the readily available sulphur ylides, which are able to transfer a methylene group to the polar double bonds of many unsaturated compounds to form cyclopropane derivatives. Examples are dimethylsulphonium methylide $(CH_3)_2\overset{+}{S}-\overline{C}H_2$ (I),[9-12] dimethylsulphoxonium methylide $(CH_3)_2\overset{+}{S}(O)-\overline{C}H_2$ (II),[13,14] aryldimethylaminosulphoxonium methylides $ArN(CH_3)_2.\overset{+}{S}(O)-\overline{C}H_2$ (III),[15,16] methyldialkylamino-oxosulphonium methylides $(CH_3).NAlk_2\overset{+}{S}(O)-\overline{C}H_2$ (IV),[17] etc. Among the suggested ylides, (II) and the highly reactive (IV) have been most widely used. Cyclopropanes can be synthesised also by means of functionally substituted sulphylides, such as dimethylsulphonium phenacylide $(CH_3)_2\overset{+}{S}-\overline{C}H.CO.C_6H_5$ (V),[18-20] methylphenylsulphonium phenacylide (VI),[21,22] dimethylsulphonium alkoxycarbonylmethylides $(CH_3)_2\overset{+}{S}-\overline{C}H.COOR$ (VII),[23-26] etc. Thus both mono- and poly-functional cyclopropanes can be synthesised by the use of sulphylides. Of course, not all the proposed sulphylides are synthetically equivalent. For example, the sphere of action of the methylide (I) is restricted to esters and amides of $\alpha\beta$-unsaturated carboxylic and sulphonic acids[27]. Thus ethyl cinnamate reacts with the ylide (I) to form ethyl *trans*-2-phenylcyclopropane carboxylate in 54% yield. Similarly, *trans*-2-phenylethylenesulphonic esters and amides are converted into those of *trans*-2-phenylcyclopropanesulphonic acid[27]:



(R=OAr, NR_2)

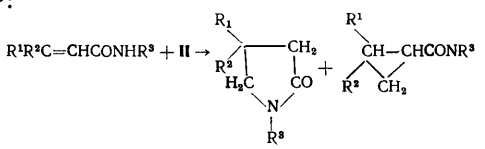
$\alpha\beta$-Unsaturated aldehydes and ketones react with (I) to form oxirans[11,12,14].

The methylide (II) is able to react also with esters of $\alpha\beta$-unsaturated mono- and di-carboxylic acids[10,28-31] to form high yields of esters of cyclopropane-mono- and -di-carboxylic acids. It is interesting that esters of diene acids react preferentially at the $\alpha\beta$-position. When a large excess of the methylide (II) is used, however, the diadduct can also be obtained[32]:



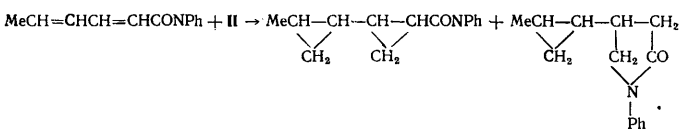
It must be emphasised that optically active 3-arylpropene-2-carboxylic esters yield optically active 2-arylcyclopropanecarboxylic esters on reaction with (II).[33] For example, (−)-menthyl and (+)-bornyl esters of cinnamic, *o*- and *p*-methoxycinnamic, and other acids react in this way.

Nitriles and amides of $\alpha\beta$-unsaturated acids also react with the methylide (II).[28,30,31,34] The former give nitriles of cyclopropanecarboxylic acids. Thus a 52% yield of 2-phenylcyclopropyl cyanide has been obtained from cinnamonitrile. Depending on their structure, amides will form amides of cyclopropanecarboxylic acids[35], pyrrolidones[30,34], or mixtures of an amide and a pyrrolidone[30,35]:

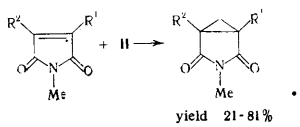


			(VIII) Yield, %	(IX) Yield, %
R^1	R^2	R^3		
H	H	H	50	0
Ph	H	H	0	40
Me	H	Ph	80	11

Sorbanilide forms a mixture[30,35]:

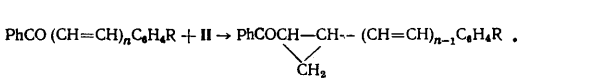


Reaction takes place between α-aryl-*N*-methylmaleimides and (II) without complications[34]:



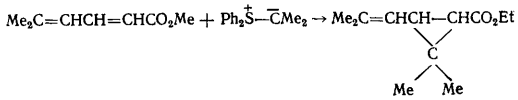
yield 21-81%

The reaction of conjugated ketones with the ylide (II), in contrast to that with (I), usually gives cyclopropyl ketones (aldehydes also form oxirans). Thus 5-methylhex-3-en-2-one and 3,6-dimethylhept-3-en-2-one are converted into the corresponding cyclopropyl ketones in 35–80% yields[30,31]. Alkyl aryl ketones—1-phenylbut-2-en-1-one[36] and chalcones[14,37]—react similarly, to give good yields of *trans*-aryl-2-benzoylcyclopropanes. In the case of vinylogues of chalcones reaction occurs at the double bond adjacent to the carbonyl group[37]:



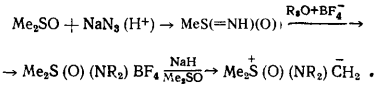
Use of the dideuterated methylide (II) enables aryl-2-benzoyl-3,3-dideuterocyclopropanes to be obtained[38,39].

The very reactive diphenylsulphonium isopropylide can be used for the synthesis of *gem*-dimethylcyclopropane systems having carbonyl functions[40]. A good yield of methyl (±)-*trans*-chrysanthemate has been obtained in this way[40]:



Methyl 2,2-dimethylcyclopropanecarboxylate (yield 71%) has been obtained similarly from methyl acrylate, dimethyl *cis*- and *trans*-3,3-dimethylcyclopropane-1,2-dicarboxylates (yields 75% and 82%) have been obtained from dimethyl maleate and fumarate respectively, etc.

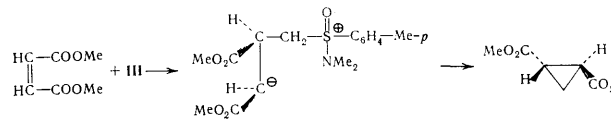
Use of the ylides (III) (Ar = C_6H_5) [15,16] and especially (VI) [17,41] has been recommended during recent years for the synthesis of functionally substituted cyclopropanes. These are readily accessible reagents, formed from dimethyl sulphoxide:



Cyclopropanes are easily formed by means of (III) and (IV) from cinnamic esters, mesityl oxide, benzylidenacetophenone, cyclohexenone, cinnamonitrile, phenyl styryl sulphone, etc. in yields of 50–98%. However, the main reaction product obtained from acrylo-*p*-toluidide is *N*-*p*-tolylpyrrolid-2-one.[30]

Use of the optically active (*R*)(−)-dimethylamino-oxo-*p*-tolylsulphonium methylide enables optically active cyclopropanes to be obtained in a quite high degree of optical purity. Thus the reaction of this ylide with methyl cinnamate gives methyl *trans*-(1*S*, 2*S*)-(+)-2-phenylcyclopropanecarboxylate in 76% yield with 30.4% optical purity[42].

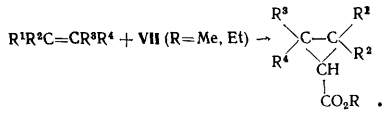
The reaction with sulphylides involves the intermediate formation of a betaine, which is confirmed by the formation of a single product—dimethyl *trans*-(1*S*, 2*S*)-cyclopropane-1,2-dicarboxylate (yield 50%, optical purity 17.8%)—on addition of the optically active ylide (III) (R = *p*-$CH_3C_6H_4$) to dimethyl maleate:



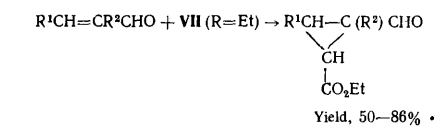
Formation of a *trans*-isomer from an initial *cis*-compound might have been explained by rotation about the single bond in the intermediate betaine, provided that formation of the latter was reversible. However, the above ylide (III) is able to isomerise dimethyl maleate into dimethyl fumarate[42].

Among the functionally substituted ylides (V)–(VII) the ethoxycarbonylide (VII) has found most extensive application during recent years, and provides an easy route to polyfunctionally substituted cyclopropanes. The ylide (VII) (R = C_2H_5) reacts readily with $\alpha\beta$-unsaturated esters (acrylic, methacrylic, crotonic, etc.), $\alpha\beta$-unsaturated ketones (methyl vinyl ketone, mesityl oxide), and nitriles (acrylonitrile) to form 45–90% yields of the corresponding

cyclopropanes when the reaction is conducted in an aprotic solvent (acetone, benzene, dichloromethane) at 45—80°C:[23-25,43]



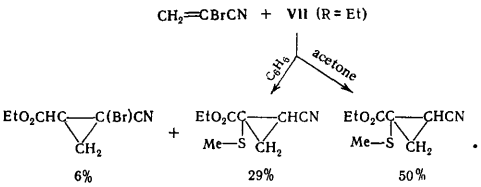
A most interesting feature of this ylide (VII) is that it reacts with $\alpha\beta$-unsaturated aldehydes, not at the carbonyl group like all other sulphylides, but at the double bond to form aldehyde derivatives of cyclopropane:



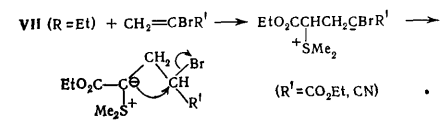
Yield, 50—86%.

Only acylic derivatives are obtained when the reaction is conducted in alcohol[44].

It is interesting that reaction of the ethoxycarbonylide (VII) with 2-bromoethyl acrylate in benzene forms a mixture of diethyl 1-bromocyclopropane-1,2-dicarboxylate and 1-methylthiocyclopropane-1,2-dicarboxylate (yields 36% and 25%), whereas in acetone only the latter product is formed in 52% yield. Reaction with α-bromoacrylonitrile occurs similarly:

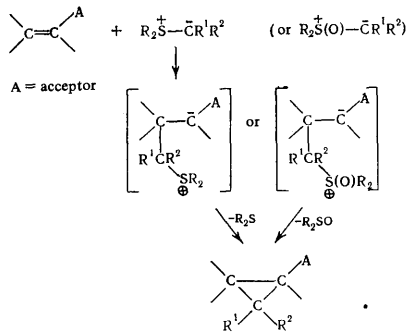


This can be explained by nucleophilic displacement in the intermediate betaine in polar solvents[24]:



The ylide (VI) reacts similarly to **VII** with $\alpha\beta$-unsaturated esters and ketones[21,22]. 1,2-Dibenzoyl-3-phenylcyclopropane (yield 77%) and 1,2,3-tribenzoylcyclopropane have been obtained by its use[20].

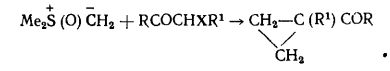
Methylene transfer is usually regarded as nucleophilic addition of the sulphylide at the polar double bond followed by elimination of a sulphide or a sulphoxide:



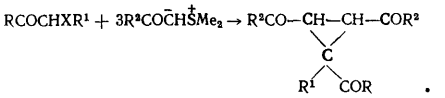
Transfer involving formation of a carbene is possible in certain special cases, e.g. in the decomposition of benzyldiphenylsulphonium tetrafluoroborate by the action of n-butyl-lithium in the presence of acenaphthylene in oxolan at −40°C with the formation of an isomer of 2-phenylphenalene[45], in the thermal decomposition of phenacyldimethylsulphonium bromide in the presence of cyclohexene with the formation of 7-benzoylbicyclo[4,1,0]heptane[18], and in the thermal decomposition of dimethylsulphonium aroylylides to 1,2,3-triaroylcyclopropanes[46].

In most cases transfer of the methylene group of sulphylides occurs stereospecifically with exclusive formation of *trans*-isomers[28,32,36-39,47]. Sometimes, however, e.g. in the reaction of the ylides (IV) with cinnamonitrile, a mixture of *cis*- and *trans*-isomers is formed (21% + 79%).[17] Similarly, the action of the ylide (VII: R = C_2H_5) on methacrylaldehyde give a mixture of *cis*- and *trans*-isomers in the proportions 68:2, with acrylaldehyde and crotonaldehyde the mixture contained 17—18% of the *cis*-isomer, with methyl vinyl ketone 2%, ethyl acrylate 3%, and methyl acrylate 9%. Chalcone, however, gave a mixture of roughly equal quantities of *cis*- and *trans*-isomers[43].

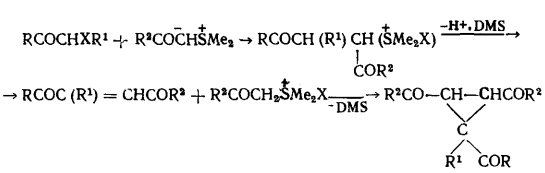
The use of sulphylides in the synthesis of cyclopropanes is not confined to reaction with activated double bonds. It was observed[22] in 1966 that the ylide (VI) reacts with bromoacetic ester in chloroform to give ethyl 2,3-dibenzoylcyclopropanecarboxylate, though in only 4,1% yield. It has since been suggested[48,49] that cyclopropyl ketones and cyclopropanecarboxylic esters can be synthesised by the action of the ylide (II) on α-halogenoketones (1-bromo-3,3-dimethylbutan-2-one, 2-chlorocyclohexanone, ω-bromoacetophenone, 2α-chlorotestosterone acetate, etc.) and on esters of α-halogenated acids (ethyl α-bromobutyrate, methyl α-bromo-α-phenylacetate):



The reaction is conducted with excess of the ylide in oxolan at −20° to −30°C, and the yields vary from 13% to 40%. The use of ylides of type (VI) enables trisubstituted cyclopropanes to be synthesised[50]:



Yields are 65—87% with bromo-ketones and phenacylides, and vary from 50% to 90% with alkoxycarbonylides. The probable reaction scheme



was suggested[50].

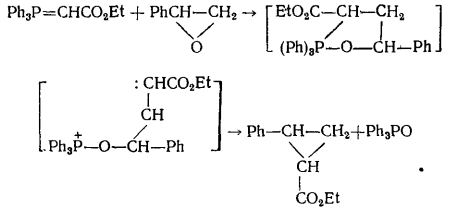
A further route for synthesising polyfunctional cyclopropanes by means of sulphylides is the reaction between mono- or di-substituted vinyldimethylsulphonium methyl sulphates $R^1.CH:CR.S(CH_3)_2CH_3SO_4$ and sodium derivatives of acids in alcoholic solution at 0°C:[51-53]



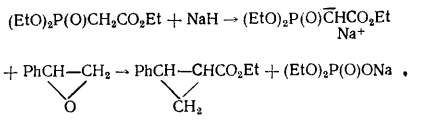
This method has been used to obtain 1,1-dicyano-2-phenylcyclopropane (yield 30%) from malononitrile, ethyl 1-cyano-2-phenylcyclopropanecarboxylate (60%) from

cyanoacetic ester, diethyl 2-phenylcyclopropane-1,1-dicarboxylate (60%) from malonic ester, etc. In every case only the *trans*-derivative was formed[53].

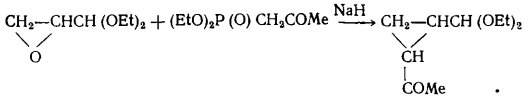
Phosphonium ylides also can be used for synthesising functionally substituted cyclopropanes, but to a limited extent. The most interesting method is the reaction of stable phosphonylides with epoxides[54-56], first described in 1962.[54] Thus ethyl triphenylphosphoranylidenacetate reacts with the α-oxides of oct-1-ene, cyclohexene, and styrene to form the corresponding cyclopropanecarboxylic esters and triphenylphosphine oxide. When styrene *l*-(−)-α-oxide is used, the optically active *trans*-cyclopropane is formed, though in low optical yield:



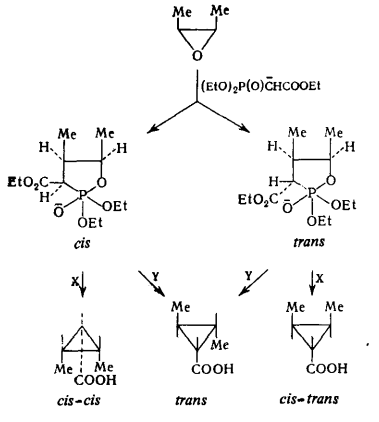
Phosphonate carbanions react similarly to phosphoranes with α-oxides of alkenes[57-61]. Thus ethyl diethoxyphosphinylacetate reacts with phenyloxiran in the presence of sodium hydride in diglyme at 85°C to form ethyl 2-phenylcyclopropanecarboxylate (yield 42%):[57]



A most interesting example is the synthesis of the acetal of 1-acetyl-2-formylcyclopropane in 60% yield[62] by the reaction of diethyl acetonylphosphonate with 2-diethoxymethyloxiran in the presence of sodium hydride in diglyme at 100—110°C:

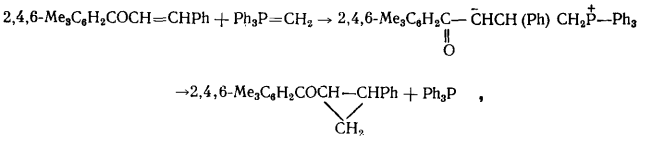


Fairly detailed investigations[54,58,63,64] led to the following mechanism for the reaction of phosphonates with oxides:



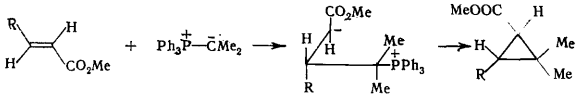
Such a scheme is supported by a study of the reaction of optically pure *trans*-(+)(2*R*, 3*R*)-2,3-dimethyloxiran and of the corresponding *cis*-isomer with ethyl diethoxyphosphinylacetate[64], to give after hydrolysis of the optically active *trans*-isomer a mixture of 90% of *trans*-(+)(2*S*, 3*S*)-2,3-dimethylcyclopropanecarboxylic acid, 6% of *cis*-2,*cis*-3-dimethylcyclopropanecarboxylic acid, and 1% of *cis*-2,*trans*-3-dimethylcyclopropanecarboxylic acid; the *cis*-isomer gave a mixture of 4% of racemic *trans*-2,3-dimethylcyclopropanecarboxylic acid, 6% of the *cis*,*cis*-isomer, and 90% of the *cis*,*trans*-isomer. Such proportions are explained by the relative quantities of intermediate cyclic products and(or) the relative possibility of X processes (direct decomposition of the intermediate ring by a synchronous mechanism or via a zwitterion) and Y processes (ring opening followed by attack from the rear); in the opening of the *cis*-oxide they undoubtedly represent steric control of the reaction after opening of the phosphonate ring.

Phosphylides can in some cases react also with $\alpha\beta$-unsaturated aldehydes and ketones to form cyclopropanes, not alkenes. Thus methylenetriphenylphosphorane reacts with mesityl α-styryl ketone[65] to form mesitoyl-2-phenylcyclopropane and triphenylphosphine:

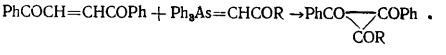


Steric hindrance by the mesityl group probably prevents reactions at the carbonyl group.

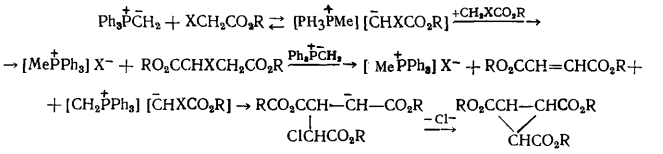
A convenient synthesis of *trans*-2,2-dimethylcyclopropanecarboxylic esters is based on the 1,4-addition of triphenylphosphonium isopropylide to *trans*-$\alpha\beta$-unsaturated esters followed by cyclisation of the intermediate with elimination of triphenylphosphine[66]:



Stable arsenic ylides react[67] with fumaric ester and *trans*-dibenzoylethylene to give good yields of the difficultly accessible 1,2,3-trisubstituted cyclopropanes in which all three substituents are electron-accepting:

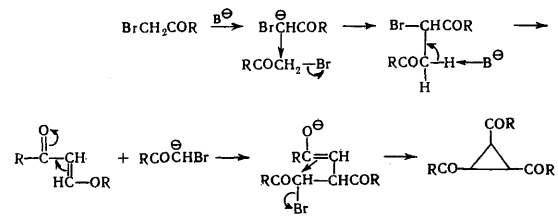


Certain phosphylides react with esters of α-halogenated acids to form trialkyl cyclopropane-1,2,3-tricarboxylates[68,69], for which the scheme

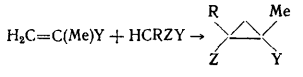


was suggested. The phosphylide thus acts as a base analogous to potassium t-butoxide, whose action on α-chloroacetamide gives *trans*-cyclopropanetricarboxamide[70]. Similar changes are produced also by the action

of lithium in liquid ammonia on ethyl bromoacetate[71] or of sodium hydride in Hexametapol on benzyl bromides or halogeno-acetic esters[72,73]:

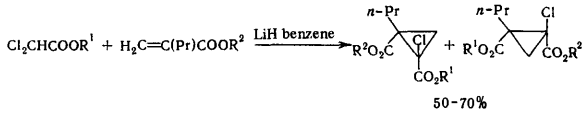


The formation of unsaturated compounds during the reaction is confirmed by the fact that ethyl bromoacetate reacts with ethyl acrylate or diethyl fumarate under the same conditions to form respectively diethyl cyclopropane-*trans*-1,2-dicarboxylate (yield 32%) and triethyl cyclopropane-*trans*-1,2,3-tricarboxylate (64%).[73] Thus the above reactions represent a particular case of the synthesis of cyclopropanes by the interaction of unsaturated compounds, activated by electron-accepting substituents (alkoxycarbonyl, cyano), with α-halogenated acids, ketones, or nitriles in the presence of hydrides or alkali-metal alkoxides[74-79]:



The isomer in which the electron-accepting groups activating the initial molecules are arranged in mutually *cis*-positions is often the principal or even the only product in this reaction. Thus methyl methacrylate reacts with methyl chloroacetate to give a 69—71% yield of a mixture of 93% of *cis*- and 7% of *trans*-dimethyl 1,2-dimethylcyclopropane-1,2-dicarboxylates; with methyl dichloroacetate only dimethyl *cis*-1-chloro-2-methylcyclopropane-1,2-dicarboxylate is obtained, in 74% yield. However, the reaction of methyl methacrylate with ethyl iodoacetate gives a 21% yield of a mixture of equal quantities of *cis*- and *trans*-isomers[74].

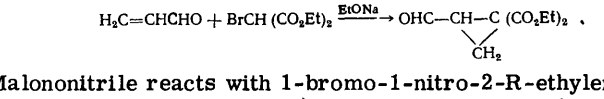
This method has recently undergone further development. Esters formed with different alcohols can be used, e.g. ethyl dichloroacetate and methyl α-propylacrylate, to give cyclopropanedicarboxylic esters with different alkyls[80]:



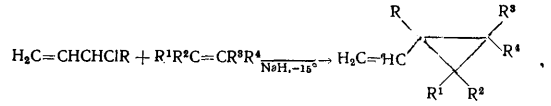
50-70%

The reaction is especially selective when an alcohol corresponding to the dichloroacetate is used to decompose the reaction mixture.

α-Unsaturated aldehydes also undergo this reaction. Thus acrylaldehyde and ethyl bromomalonate in the presence of sodium ethoxide give a 50% yield of diethyl 2-formylcyclopropane-1,1-dicarboxylate[81]:



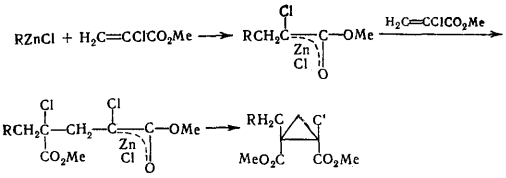
Malononitrile reacts with 1-bromo-1-nitro-2-R-ethylenes (R = C_2H_5, C_6H_5, p-$NO_2C_6H_4$) to form 1,1-dicyano-2-nitro-3-R-cyclopropanes[82]. Substituted vinylcyclopropanes can be obtained by applying the reaction to derivatives of 2-chlorobut-3-enoic acid[83]:



(R=CO_2Me, CN; R^4=COOMe, CN)

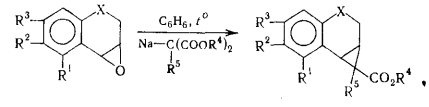
The stereochemistry of this reaction is controlled by the solvent: the formation of *cis*-isomers is favoured by solvents of low dielectric constant, and that of *trans*-isomers by solvents of high dielectric constant. In the reaction of 2-chlorobut-3-enonitrile with methyl acrylate in toluene, for example, methyl 2-cyano-2-vinylcyclopropanecarboxylate is formed with a total yield of 33%, comprising a 73 : 27 mixture of *cis*- and *trans*-isomers; when the reaction is conducted in Hexametapol the same cyclopropane is formed in 41% yield, comprising a 13 : 87 mixture.

A method proposed recently for synthesising cyclopropanedicarboxylic acids is based on the reaction of 2 moles of an α-chloroacrylate with 1 mole of an alkylzinc halide[84-87], and also enables *cis*-isomers to be obtained:



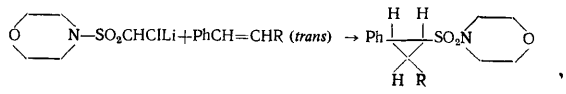
Partial asymmetric synthesis can be effected by the use of an optically active alkylzinc methoxide or a mixture of diethylzinc and an optically active alcohol (*l*-menthol).

Another new reaction for the formation of a cyclopropane ring consists in the nucleophilic opening of an oxide in the presence of a sodiomalonic ester in a non-polar medium[88,89]:



(X = CH_2, O) yield 37-64%

Addition of α-chloromorpholinosulphonylmethyl-lithium to an activated double bond to yield a cyclopropane[90] may be of interest:

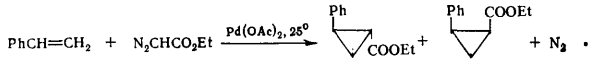


(R=SO_2Ph, CN, NO_2) yield 21-73%

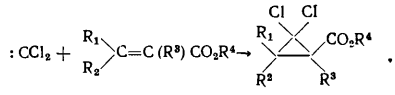
Such are the new synthetic methods which are of interest for the preparation of functionally substituted cyclopropanes. In addition, traditional methods have undergone further development, Firstly, unsaturated compounds have been treated with carbenes, which behave as electrophilic reagents[91]. Synthesis is based mainly on the addition of carbenes to functionally substituted alkenes. Functionally substituted carbenes—phenoxycarbene[92-96], alkoxycarbenes[97-100], selenocarbenes[10] sulphocarbenes[102,103], dicyanocarbenes[104-107], and several others—are seldom used in cyclopropane formation, with the exception of ethyl carbenecarboxylate[108-113].

As in previous years the main sources of carbenes have been diazo-compounds and polyhalogenated derivatives, with published methods of cyclopropane synthesis differing

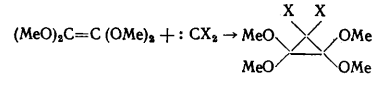
mainly in the mode of generation of the carbenes. It has been suggested that catalysts—copper powder[2,114,115], palladium acetate[116]—should be added to the diazo-compounds, in addition to the usual processes. Thus 2,4-dimethylpent-2-ene reacts with diazoacetic ester in the presence of copper powder to give ethyl 2-isopropyl-3,3-dimethylcyclopropanecarboxylate in 54% yield[2]. Similar methods of preparation have been used for *cis,cis*- and *trans,trans*-2-aryl-3-methylcyclopropanecarboxylic acids and esters[114], as well as for ethyl 2-methyl-3-propenylcyclopropanecarboxylates[115]. The corresponding cyclopropanes are formed by the action of diazoacetic ester on alkenes in the presence of palladium acetate in hexane[116]:



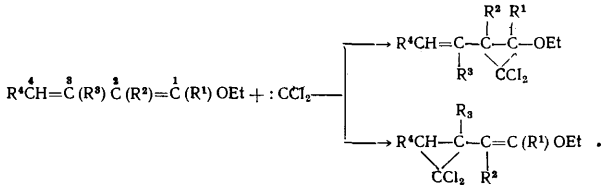
Dihalogenocarbenes have recently found fairly wide application for the synthesis of functionally substituted cyclopropanes. Besides traditional methods of generation (action of aqueous alkalis or alkoxides on polyhalogeno-derivatives) it has now been suggested that they should be generated by the action of aqueous caustic soda on polyhalogeno-derivatives in the presence of benzyltriethylammonium chloride as catalyst. The dichlorocarbene produced in this way adds e.g. at the double bond in $\alpha\beta$-unsaturated acids to form dichlorocyclopropanecarboxylic esters[117]:



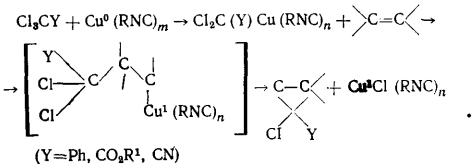
Interesting new examples have also been reported of the synthesis of functionally substituted cyclopropanes by means of dihalogenocarbenes. Thus dichlorocarbene adds at the double bond in acrylaldehyde diethyl acetal to form 1,1-dichloro-2-diethoxymethylcyclopropane in 33% yield[118]. An analogous reaction takes place with tetramethoxyethylene to give good yields of 1,1-dihalogeno-2,2,3,3-tetramethoxycyclopropanes[119]:



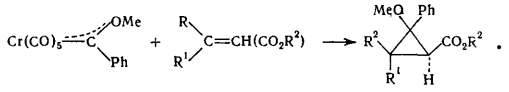
1-Ethoxybuta-1,3-dienes are also able to add dichlorocarbene. The reaction occurs non-stereospecifically, predominantly (67—100%) at the 3,4-double bond to give a mixture of substituted 1,1-dichloro-2-ethoxycyclopropanes (*trans*-1,2,*trans*-3,4 and *trans*-1,2,*cis*-3,4) in 20—40% yield[120]:



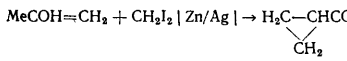
Polyhalogeno-derivatives can be used in other ways for the synthesis of cyclopropanes. Thus it has recently been suggested that alkenes having an electron-deficient double bond should be treated with copper carbenoid derivatives obtained by the reaction of trichloromethyl derivatives with copper and isocyanides[121,122]:



Functionally substituted cyclopropanes can be synthesised by the reaction of $\alpha\beta$-unsaturated esters with carbene complexes of transition-metal carbonyls.[123] For example, the complex of methoxy-phenylcarbene with chromium pentacarbonyl reacts stereospecifically when heated with *trans*-cinnamic, fumaric, and maleic esters to give 2-methoxy-2-phenylcyclopropane-mono- and -di-carboxylic esters:



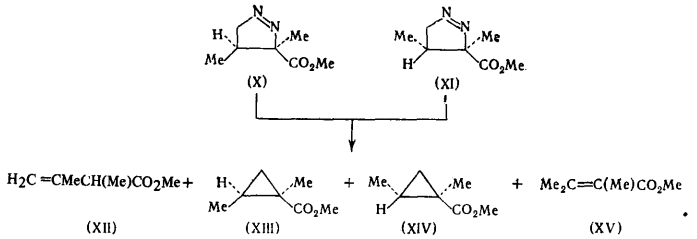
Several improvements have been introduced also into one of the oldest syntheses of cyclopropanes—the Simmons—Smith reaction. Thus an improved modification has recently been suggested in which the zinc—copper couple has been replaced by a zinc—silver couple, which enables functionally substituted cyclopropanes to be obtained in higher yields than by the original method. For example[124]



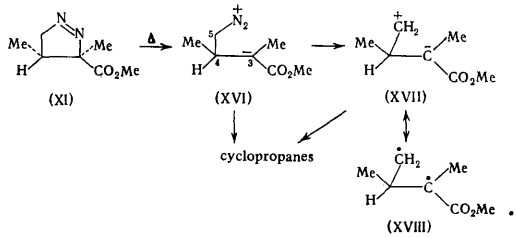
The Simmons—Smith reagent can be used[125] for the partial asymmetric synthesis of cyclopropanes from (−)-menthyl esters of $\alpha\beta$- and $\beta\gamma$-unsaturated carboxylic acids. Optically active *trans*-2-methylcyclopropanecarboxylic acid (yield 20—35%), *trans*-2′-methylcyclopropylacetic acid (54.5%), methyl *trans*-2-phenylcyclopropanecarboxylate (7—33%), and other derivatives have been obtained by this method[125].

The pyrolysis of pyrazolines is widely used to obtain cyclopropanes, and has been discussed in detail in several reviews[8,126,127]. We shall consider below only the most interesting new examples of the preparation of functionally substituted cyclopropanes by this method. Firstly, a detailed study by gas—liquid chromatography of the pyrolysis of methyl *cis*- and *trans*-3,4-dimethyl-Δ^1-pyrazoline-3-carboxylates showed[128] that, contrary to the widely held view, the configuration of the original molecule is in several cases not preserved in the thermal cleavage of Δ^1-pyrazolines, and the process is more complicated. For example, the pyrolysis of both *trans*- and *cis*-isomers (X) and (XI) gives a mixture of methyl 2,3-dimethylbut-3-enoate (XII), methyl *trans*-1,2-dimethylcyclopropanecarboxylate (XIII), methyl *cis*-1,2-dimethylcyclopropanecarboxylate (XIV), and methyl 2,3-dimethylbut-2-enoate

(XV), in the respective proportions 0.15 : 1.22 : 1.00 : 1.16 (X) and 0.24 : 0.70 : 1.00 : 3.73 (XI):



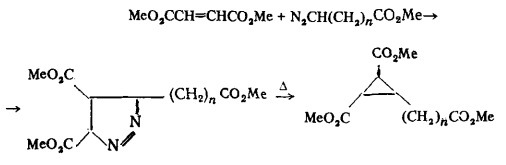
Since both mechanisms (ionic and biradical) suggested earlier for the thermal cleavage of Δ^1-pyrazolines involve preservation of the initial configuration, the non-stereospecificity observed in the above example was explained[128] on the assumption that the intermediate (XVI) is first formed, and is then converted with the loss of nitrogen into the intermediate (XVII), whose cyclisation yields the cyclopropanes:



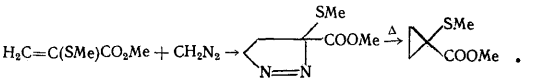
Loss of stereospecificity may result from free rotation about the $C_{(3)}-C_{(4)}$ bond, most probably in (XVI), since (XVII), which may resonate with the biradical (XVIII), would cyclise extremely rapidly.

Several new examples of the preparation primarily of cyclopropanemonocarboxylic acids and their derivatives by the pyrolysis of Δ^1-pyrazolines have been described during recent years[129-132]. Thus methyl 1-methylcyclopropanecarboxylate (yield 63%) has been prepared from methyl methacrylate via the corresponding Δ^1-pyrazoline; and a mixture of ethyl *cis*- and *trans*-2-phenylcyclopropanecarboxylates[133] from substituted styrenes and diazoacetic ester.

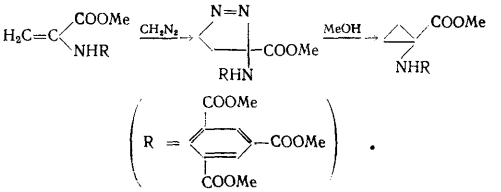
Furthermore, various cyclopropanes containing two carboxy-groups—in the ring or in the ring and in the side-chain—have been obtained by the thermal decomposition of Δ^1-pyrazolines from esters of unsaturated dicarboxylic acids[134-137]. The addition of ω-diazoalkanoic esters $N_2CH[CH_2]_nCOOCH_3$ ($n = 1-4$) to esters of unsaturated dicarboxylic acids is especially interesting, and leads to the formation of Δ^1-pyrazolinetricarboxylic acids, whose thermal decomposition gives cyclopropanetricarboxylic esters[138,139]:



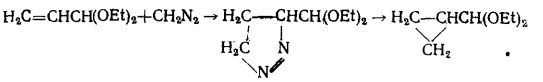
A few examples have also been reported of the preparation of cyclopropanecarboxylic acids containing other functional groups. Thus the Δ^1-pyrazoline obtained from methyl α-methylthio-acrylate and diazomethane is converted when heated (50°C) into methyl 1-methylthiocyclopropanecarboxylate[140]:



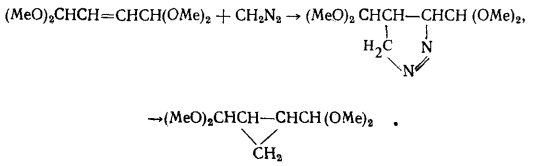
Similarly, boiling in methanol the Δ^1-pyrazoline from the tetramethyl ester of α-2, 4, 6-tricarboxyanilinoacrylic acid and diazomethane gives the tetramethyl ester of *N*-1′-carboxycyclopropylaniline-2, 4, 6-tricarboxylic acid[141,142]:



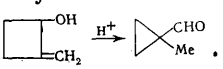
The Δ^1-pyrazoline from acrylaldehyde acetal and diazomethane is converted by pyrolysis at 400—450°C and 1 mm pressure into the acetal of cyclopropanaldehyde[143]:



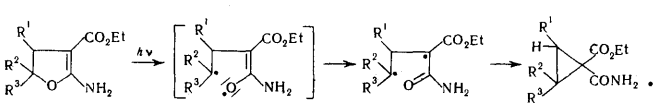
A method has been worked out[144] also for preparing 1, 2-bisdimethoxymethylcyclopropane[144] by the decomposition under similar conditions of 3, 4-bisdimethoxymethyl-Δ^1-pyrazoline, obtained from the easily accessible diacetal of fumaraldehyde and diazomethane, the yield reaching 93%:



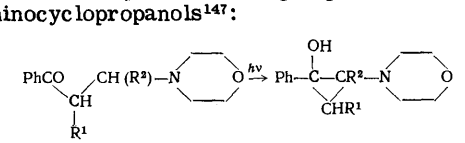
A few cases have been reported in which functionally substituted cyclopropanes have been formed in other ways. Thus heating 2-alkylidenecyclobutanols in a sealed tube or with 5% sulphuric acid converts them quantitatively into 1-alkylcyclopropanaldehydes[145]:



Irradiation of ethyl 2-amino-4, 5-dihydro-3-furoates in dioxan or oxolan in the presence of triphenylene or 2-naphthyl phenyl ketone as sensitiser yields a mixture of isomeric ethyl 1-carbamoylcyclopropanecarboxylates[146]:



Finally, the irradiation of certain 3-amino-ketones in dioxan in an atmosphere of nitrogen gives 80—95% yields of 2-aminocyclopropanols[147]:

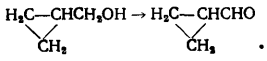


Thus almost any functional cyclopropane can be prepared by variations on the different methods available.

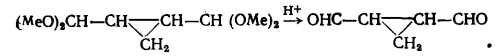
A fundamentally different method of obtaining functionally substituted cyclopropanes is to introduce functions into or to modify existing functional substituents in the cyclopropane ring, which presupposes a knowledge of the behaviour of various functional groups in the ring. Many data have been published on the reactions of cyclopropane rings involving rupture or change in the ring[7]. Considerably fewer publications have appeared on the reactions of functional groups attached directly to the cyclopropane ring. The following Section will be devoted to the most interesting new examples of such reactions.

III. SOME REACTIONS OF FUNCTIONALLY SUBSTITUTED CYCLOPROPANES

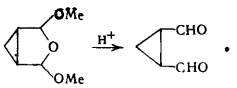
In most cases the behaviour of functional groups attached to a cyclopropane ring is almost identical with their behaviour in other classes of compounds. It has been shown during recent years, for example, that cyclopropylmethanol is oxidised to the aldehyde by hydrogen peroxide in the presence of iron(II) salts[148], aluminium isopropoxide[149], and also 1*N* aqueous ammonium cerium nitrate[150] (in the last case the yield of the aldehyde reaches 64%):



The acid hydrolysis of acetals of cyclopropane aldehydes goes in the usual way. Thus the diethyl acetal of cyclopropanaldehyde gives a 50% yield of the aldehyde when heated with 1*N* trichloroacetic acid[143]. The diethyl acetal of 2,2-dichlorocyclopropanaldehyde is hydrolysed, when heated with 12% sulphuric acid, to give a 50% yield of the corresponding aldehyde[118]. Finally, the hydrolysis of 1,2-bisdimethoxymethylcyclopropane gives, on heating with 6% phosphoric acid and removal of the resulting methanol by distillation, a 60% yield of cyclopropane-*trans*-1,2-dialdehyde[144] (the use of other acids or other conditions led to resinification and decomposition of the final hydrolysis product):



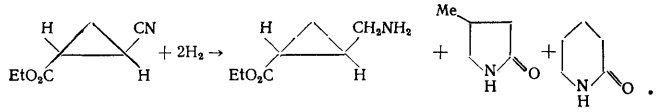
Hydrolysis of 2,4-dimethoxy-3-oxabicyclo[3,1,0]hexane even yielded the very unstable cyclopropane-*cis*-1,2-dialdehyde[151,152]:



Cyclopropyl cyanide undergoes fairly smooth reduction to cyclopropanaldehyde by the action of lithium hydrotriethoxyaluminate[153] or lithium hydrotri-n-butoxyaluminate[153]; and amides of cyclopropanecarboxylic acids, e.g. the ethylenamide[154] and the dimethylamide[155], are reduced quite smoothly by lithium tetrahydroaluminate, dihydrodiethoxyaluminate, or hydrotriethoxyaluminate. Yields of the aldehyde reach 20–60%, but, since it reacts under alkaline conditions, it can generally be isolated only as the 2,4-dinitrophenylhydrazine.

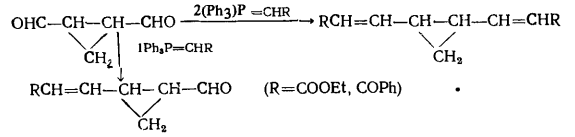
Cyclopropanecarbonyl chloride is reduced by lithium dihydrodi-t-butoxyaluminate to the aldehyde[154] (isolated only as the 2,4-dinitrophenylhydrazone). Similarly, Rosenmund reduction of cyclopropane-1,2-dicarbonyl dichloride gave cyclopropane-1,2-dialdehyde[156] (which also could be isolated only as the 2,4-dinitrophenylhydrazone).

The cyclopropane ring is preserved when ethyl *trans*-2-cyanocyclopropanecarboxylate undergoes catalytic reduction over Raney nickel under 50 atm at 35–37°C to ethyl 2-aminomethylcyclopropanecarboxylate[157]:



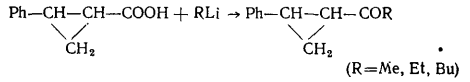
Boron hydride complexes reduce *N*-alkylidenecyclopropylamines only at the alkylidene group to the corresponding *N*-substituted cyclopropylamines in 70–90% yields[158].

Condensation of *trans*- and *cis*-2-phenylcyclopropanaldehydes goes normally with the sodium derivatives of phosphonacetic ester or benzylphosphonate to form ethyl *trans*- and *cis*-β-2-phenylcyclopropyl-α-R-acrylates (yield 50–60%).[159] Similarly, the condensation of dimethyl 2-formylcyclopropane-1,1-dicarboxylate with dimethyl 2-oxoheptylphosphonate gives a 70% yield of the αβ-unsaturated ketone[160]. Cyclopropane-1,2-dialdehyde also reacts with phosphonacetic ester, giving a 50% yield of diethyl cyclopropane-1,2-bis-α-R-β-acrylate[144]. Phosphonacetophenone and phosphonacetonitrile do not react with cyclopropane-1,2-dialdehyde under these conditions. The dialdehyde reacts normally under the conditions of the Wittig reaction, being converted by ethyl triphenylphosphoranylidenacetate and by phenyl triphenylphosphoranylidenemethyl ketone into products in which one or both aldehyde groups have reacted depending on the proportions of the reactants (yields 33–45%).[144]

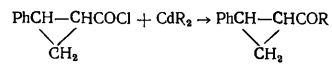


It is interesting that the condensation of phosphonacetic ester with dibenzoylcyclopropane in the presence of sodium hydride involves only one of the carbonyl groups even in the presence of excess of the reagent, and gives ethyl β-2-benzoylcyclopropylcinnamate[156].

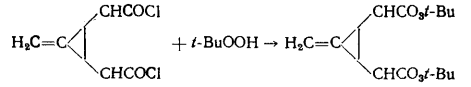
Treatment of the stereoisomeric 2-phenylcyclopropanecarboxylic acids with an alkyl-lithium under ordinary conditions gave the cyclopropyl ketones[161]:



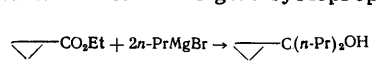
A dialkylcadmium converts cyclopropanecarbonyl chlorides also into ketones[161]:



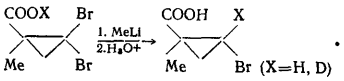
It is interesting that the action of t-butyl hydroperoxide on 3-methylenecyclopropane-1,2-dicarbonyl dichloride in pyridine gives a 70% yield of the di-t-butyl bisperoxycarboxylate[162]:



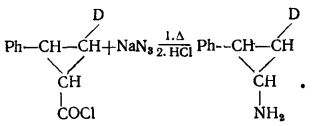
Ethyl cyclopropanecarboxylate reacts normally with *n*-propylmagnesium bromide to give cyclopropyldipropylmethanol[163]:



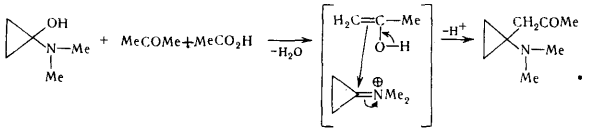
It is interesting that methyl-lithium causes stereoselective reduction of the bromine atom in the *cis*-position relative to the carboxyl in 2,2-dibromo-1-methylcyclopropanecarboxylic acid[164]:



Azides of stereoisomeric 2-deutero-3-phenylcyclopropanecarboxylic acids undergo the usual rearrangement to amines when heated[165]:

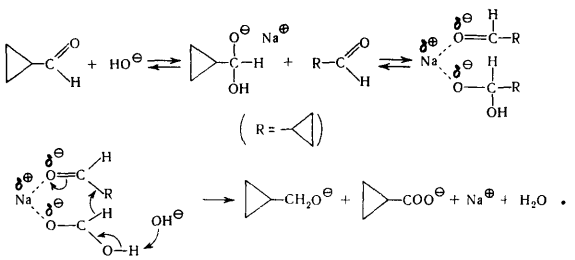


A Mannich base is obtained when 1-dimethylaminocyclopropanol is heated with acetone and acetic acid (at 65°C for 20 h):[166]



Acid hydrolysis of α-cyclopropyl-β-methoxystyrene goes normally to α-cyclopropylphenylacetaldehyde, which condenses in the usual way with but-3-en-2-one to give 4-cyclopropyl-4-phenylcyclohex-2-enone[167].

It has recently been shown that cyclopropanaldehyde, which contains an α-hydrogen atom, undergoes not an aldol condensation but the Cannizzaro reaction on treatment with aqueous alkali, with the formation of cyclopropylmethanol and cyclopropanecarboxylic acid. This is a second-order reaction with respect to aldehyde and alkali, and exhibits a small positive salt effect. Together with the absence of a deuterated cyclopropylmethanol when the reaction is conducted in heavy water, this suggests the reaction mechanism[168]



It is interesting that cyclobutanaldehyde forms aldol condensation products when treated with aqueous alkali[169].

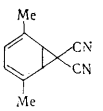
Thus functionally substituted cyclopropanes exhibit not only trivial behaviour but also unusual reactions, perhaps a consequence of structural peculiarities of the cyclopropane ring. The next Section will deal with current views on the structure of this ring system.

IV. STRUCTURE AND TRANSMISSION OF ELECTRONIC EFFECTS THROUGH THE CYCLOPROPANE RING

Cyclopropane is formally a saturated compound, in which the carbon atoms would have been in a state of sp^3 hybridisation. However, the angles between the carbon atoms in the cyclopropane ring differ markedly from those in saturated compounds. Two principal theories of the electronic structure of cyclopropane have been advanced, and examined in detail in a review[7]. According to Walsh[170] a carbon atom in cyclopropane is in a state of sp^2 hybridisation. Two sp^2 orbitals of each carbon atom form bonds with *s* orbitals of hydrogen. The remaining six electrons (two from each carbon atom) are involved in bond formation between the carbon atoms, of which four electrons belong to bonds formed by the overlapping of 2*p* orbitals, while the remaining two electrons form a three-centre orbital. This model explains the enhanced reactivity of the carbon–carbon bonds in cyclopropanes, evident in the easy rupture of the ring. The intensified *p*-character of the bonds in cyclopropane is confirmed by dipole moments and quadrupole magnetic resonance data obtained in a study of cyclopropyl chloride[171,172]. This model will also explain the ability of the cyclopropyl group to "conjugate" with π-electron systems, where "conjugation" implies the possibility of overlap of the three-centre orbital with π- and *p*-orbitals of a substituent (a vinyl group, a lone pair of electrons of an oxygen or a nitrogen atom, etc.)[173–175].

In the Coulson–Moffitt model[176] the carbon atoms are situated at the corners of an equilateral triangle, and hybridisation is such that two orbitals of any carbon form an angle of 104° in the plane of the ring. The carbon–carbon bonds are then curved (banana-shaped), the carbon atoms are in a state of $sp^{4,12}$ hybridisation, and the orbitals of the carbon–hydrogen bonds are in a state of $sp^{2,28}$ hybridisation[177]. The angle between the axes of the $sp^{4,12}$-hybridised orbitals is 104°.

The presence of curved bonds in cyclopropane is supported experimentally by the distribution of electron density in 7,7-dicyano-2,5-dimethylnorcaradiene



found by X-ray diffraction. The bending of the carbon–carbon bonds in the cyclopropane ring was shown to be ~20° (theoretically 22°). These results indicated also that the cyclopropane ring forms an angle of 73° with the cyclohexadiene plane[178].

Although the two models of cyclopropane are mathematically equivalent[179], the Coulson–Moffitt model permits certain predictions which cannot be made by means of the Walsh model. Furthermore, a model with curved bonds can be used to depict orbitals in those cyclopropane molecules which cannot be represented solely in terms of *sp*, sp^2, and sp^3 hybridisation.

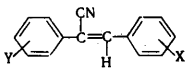
Various methods of quantum-chemical calculations have lately been used to study the electronic structure of cyclopropane[180–182]. Non-empirical calculations by the LCAO-MO self-consistent field method have established[183] that overlapping of the *d*-orbitals of the carbon atoms in the carbon–carbon bonds is possible, as well as the above two types, and should be taken into account in discussion of the hybridisation of the carbon atoms in the cyclopropane ring.

Calculations have shown that, in the ground state of cyclopropane, the highest electron density is concentrated on the carbon atoms, diminishes in the region between the hydrogen atoms attached to carbon, but is quite high between the carbon atoms along the carbon–carbon axis, and some charge is also concentrated at the centre of the ring. Thus the bonds retain a considerable *p*-character in the proposed model, which will explain the ability of the

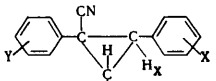
cyclopropane ring to "conjugate" with π-electron systems.

Optimum conditions for interaction between the cyclopropane ring and the *p*-orbitals of an adjacent carbon atom in the side-chain are satisfied if the plane of the ring and the axes of the *p*-orbitals are parallel[177,184-189].

The possibility of electronic interactions between the cyclopropane ring and unsaturated groups and the transmission of the effect of substituents through the ring have been studied by many chemists[170,186-192]. An induction mechanism of transmission is evidently fully applicable to the cyclopropane ring. Hitherto, however, there has been no generally accepted view on the possibility of a mesomeric mechanism of transmission of electronic effects through the ring, i.e. on the possibility of conjugation between the cyclopropane ring and multiple bonds, and this problem remains a matter of controversy.



(XX)



(XIX)

Table 1. Cyanide frequencies and reaction constants of series of cyanocyclopropanes (XIX) and cyanostilbenes (XX).

X	Y	Series (XX) ν_{CN}, cm^{-1}		Series (XIX) ν_{CN}, cm^{-1}	
p-Me_2N	H	2236.5	ρ=0.345	2207	ρ=0.250
p-Me_2N	*p*-Cl	2237		2209	
p-Me_2N	*p*-NO_2	2240		2212	
H	*p*-NO_2	2242	ρ=0.447	2220.5	ρ=0.104
p-NO_2	*p*-NO_2	2243		2226	
m-NO_2	*p*-NO_2	2243		226.5	
p-OCH_3	*p*-NO_2	2241		2218	

Table 2. Carbonyl frequencies (ν_{CO}, cm^{-1}) of *p*-R.C_6H_4.X.CO.C_6H_5 series in chloroform.

X	H	*i*-Pr	Me	F	Cl	Br	NO_2
—CH—CH \ / CH_2	1666	1668	1667	1668	1670	1668	1670
—CH=CH—	1665	1663	1662	1667	1666	1667	1670
No bridge	1660	1658	—	—	—	1660	—
—CH_2CH—	1685	—	1685	—	—	1687	—

Infrared spectroscopy, Raman spectra, nuclear magnetic resonance spectra, dipole moments, and pK_a values of acids have been used to study the interaction of a three-membered ring with adjacent unsaturated groups in the ground state. The effect of substitution on the infrared frequency of the functional group has been studied in greatest detail on 1,2-diphenylcyclopropyl cyanides, when the cyanide frequencies correlate with the α-constants of the substituents. However, the slope of the correlation graph is considerably smaller than for the corresponding series of cyanostilbenes. Furthermore, the CN frequencies in cyclopropanes are appreciably lower than that in benzyl cyanide (2256 cm^{-1}—Table 1).

Comparison of the carbonyl frequencies of 1-aryl-2-benzoylcyclopropanes and of substituted chalcones, benzophenones, and 1-aryl-2-benzoylethanes[37] (Table 2) shows that replacement of an ethylene unit by a cyclopropane ring or a vinylene fragment produces a large shift (~20 cm^{-1}) in the carbonyl frequencies, which confirms the ability of the cyclopropane ring to conjugate with the carbonyl group. However, the introduction of various *para*-substituents into the phenyl ring in 1-benzoyl-2-phenylcyclopropanes has little effect on the carbonyl frequency.

Table 3. Integral intensities of bands due to cyclopropanes and to unsaturated compounds.

Compound	Integral intensities of bands		
	C_6H_5, 1660 cm^{-1}	C=C, 1640 cm^{-1}	C=O, 1700 cm^{-1}
trans-1-Phenyl-2-vinylcyclopropane	1320	1250	–
1-Phenylbuta-1,3-diene	19600	48000	–
4-Phenylbut-1-ene	480	400	–
Ethyl *trans*-β-2-phenylcyclopropylacrylate	2900	9500	2700
Ethyl *cis*-β-2-phenylcyclopropylacrylate	1200	4500	1350
Ethyl 5-phenylpenta-2,4-dienoate	50500	16500	12000
Ethyl 3-methyl-5-phenylpent-2-enoate	590	2000	580

Raman spectroscopy was used to make very detailed studies[194,195] of the interaction of a cyclopropyl group with unsaturated side-chains. The ability of the ring to transmit the conjugation of attached groups was determined by examining the Raman spectra[196] of a series of 1-phenyl-2-R-vinylcyclopropanes and corresponding unsaturated or saturated compounds. Comparison of the integral intensities (Table 3) indicates that a three-carbon ring is able to conjugate with attached unsaturated groups and to transmit their influence provided that conformations most favourable for such conjugation are established, so that the π-orbitals of the substituent are able to overlap the Walsh three-centre orbital of the cyclopropane ring.

The proton magnetic resonance spectra of 1,2-diphenylcyclopropyl cyanides reveal[193] a correlation between the chemical shifts of the 2- and 3-hydrogen atoms and the constants of the substituents:

$$\nu(\text{Hz}) = K(0{,}4\sigma_I + 0{,}7\sigma_M) .$$

A correlation analysis established that the substituents affect the chemical shifts of the protons mainly by a mesomeric mechanism.

A comparative study of the proton magnetic resonance spectra of *trans*-1-benzoyl-2,2-dideutero-3-R-phenylcyclopropanes, *trans*-2-benzoyl-3-R-phenyloxirans, and *cis*- and *trans*-2-benzoyl-1-cyclohexyl-3-R-phenylaziridines in deuterochloroform and in benzene showed that the differences between the chemical shifts in these two solvents correlated with the σ, σ^0, and σ^+ constants of the substituents. However, the best correlation is obtained by using the Swain *F* and *R* constants (the field-effect and resonance constants respectively). Values of 25.7, 23.3, and 13.4 were found for the reaction constants ρ of the cyclopropane, oxide, and ethylenimine rings

respectively. These results agree well with a study of the ^{19}F nuclear magnetic resonance spectra of series of compounds p-F.C_6H_4.X.C_6H_4.Y, which gave the values of ρ (the slope in ppm) −2.20, 0.84, −1.21, and −1.20 according as X was CH : CH, $CH_2.CH_2$, a cyclopropane ring, or an oxide ring. However, the substituent constants σ_1 and σ^0_R found for the cyclopropyl group in a ^{19}F-n.m.r. study of m- and p-fluorophenylcyclopropanes[200] were closely similar to those for alkyl substituents. Hence it was concluded that, in the ground state of the fluorocyclopropane molecule, the phenyl and cyclopropyl groups do not interact by a mesomeric mechanism.

Table 4. Dipole moments of ketones R.C_6H_4.X.CO.C_6H_5 (in benzene at 25°C).

R	No bridge	—CH=CH—	—CH—CH— (CH$_2$)		
	μexp	μexp	μexp	μcalc	μinter
H	2.99	3.07	2.45	2.90	−0.45
Cl	2.95	2.57	1.82	1.91	−0.01
Br	2.96	2.91	1.89	1.90	−0.01
NO_2	4.23	4.16	3.68	4.10	−0.42
m-NO_2	—		3.61	4.10	−0.49
MeO	—	3.60	2.97	2.80	0.17

The very small interaction moments $\mu_{inter} = \mu_{exp} - \mu_{calc}$ indicate (Table 4) absence of appreciable conjugation between the π-electron system of the p-R.C_6H_4 group and benzoyl in *trans*-1-benzoyl-2-p-R-phenylcyclopropanes. Comparison of the dipole moments of these cyclopropanes with those of corresponding benzophenones and chalcones (Table 4) shows that introduction of the cyclopropane ring lowers the dipole moments in comparison with benzophenones, and does not increase them, as with chalcones: i.e. cyclopropyl ketones are less polar than are benzophenones[201].

Finally, pK_a values were determined for a series of *para*-substituted *trans*-2-phenylcyclopropanecarboxylic, cinnamic, and β-phenylpropionic acids in dilute aqueous solution[202] and later in 50% ethanol[203] in order to assess the ability of the cyclopropane ring to transmit electronic effects, and a correlation analysis of the data was made. The results were contradictory. In aqueous solution the series of phenylcyclopropanecarboxylic acids and the series of phenylpropionic acids had closely similar reaction constants ρ (0.182 and 0.212 respectively; for the series of cinnamic acids ρ = 0.466), which indicates absence of interaction between the phenyl group and carboxyl through the cyclopropane ring. In alcoholic solution, however, an appreciable difference was observed between the reaction constants of the two series (0.473 and 0.344 respectively for the cyclopropane and phenylpropionic series): i.e. under these conditions the cyclopropane ring transmits electronic effects appreciably better than does an ethylene bridge. This discrepancy may be due to variation in the conformation of the compounds with the solvent. Indeed, it has been known for some time[204] that the degree of ionisation of stereoisomeric cyclopropanecarboxylic acids containing one, two, or three substituents in the ring depends to a greater extent on their spatial configuration than on the polar nature of the substituents.

It is clear from the above discussion that any conclusion on the ability of the cyclopropane ring to conjugate or to transmit effects in the ground state cannot be examined without qualification to all cyclopropane systems. Nevertheless, an inductive effect—not a mesomeric effect—predominates in the ground state in the majority of examples.

An analogy between the cyclopropane ring and the double bond can very often be traced in the excited state. The problem of the conjugation of substituents and of the transmission of their electronic effects through the cyclopropane ring in the excited state was studied quite widely by means of ultraviolet spectroscopy[200-214]. The main criterion of the possibility of conjugation between the cyclopropane ring and a substituent is a bathochromic shift and intensified absorption in comparison with model compounds not containing a cyclopropane ring.

Table 5. Wavelengths λ_{max} (nm in alcohol) in the compounds $C_2H_5O.CO.CH : CH.X.CH : CH.COOC_2H_5$ in comparison with $CH_3.CH : CH.COOC_2H_5$.

X	λ_{max}	ε
No bridge	264	30300
—CH=CH—	304	46800
C_6H_4	323	46200
—CH—CH— (CH$_2$)	252	22800
MeCH=CHCO$_2$Et	206	15520

Thus the sharp bathochromic shift (4—10 nm) in the electronic spectra of 1-aryl-2-benzoylcyclopropanes in comparison with 1-benzyol-2-phenylethane indicates interaction between the benzoyl chromophore and the cyclopropane ring. However, the nature of a substituent in the benzene ring has hardly any effect on the position of the maximum of the benzoyl chromophore[37]. The presence of a bathochromic shift in the electronic spectra of compounds of general type $C_2H_5O.CO.CH : CH.X.CH : CH.COOC_2H_5$ (Table 5) indicates quite definite interaction between chromophores separated by a cyclopropane ring[144]. Bathochromic shifts (5—29 nm) [211,212] have been observed also in the electronic absorption spectra of cyclopropylacrylic esters and corresponding models containing no cyclopropane ring. The introduction of substituents capable of conjugation into a benzene ring attached to a cyclopropane ring causes bathochromic shifts and some strengthening of absorption bands[193].

Variation from 0 to 90° in the orientation of the cyclopropane ring relative to the bisecting plane in a series on conformationally rigid p-nitrophenylcyclopropanes has little effect on the electronic interaction between the cyclopropyl group and the nitrophenyl or phenyl chromophore, according to a study of the electronic spectra of such compounds. This indicates that inductive effects play the main part in these series[215]. In an interesting example of the steric suppression of conjugation of the cyclopropane ring with double bonds[216] disturbance of the arrangement of the ring in the plane of the double bonds optimum for conjugation, on the introduction of methyl groups into the ring or into a side-chain, causes hypsochromic shifts in the electronic spectra of cyclopropylacrylic esters.

Comparison of the electronic spectra of stereoisomeric 1-phenyl-2-R-cyclopropanes (R = COOH, COR', $CONH_2$, NR'_2, CH : CH.COOH, or CH : $CH.COOC_2H_5$) with the spectra of monosubstituted cyclopropanes (phenylcyclopropane and β-cyclopropylcrotonic ester) indicates that the cyclopropane ring is able to transmit the effect of attached groups, but to a less extent than can be vinylene bridge. Differences in the spectra of ethyl *cis*- and *trans*-β-2-phenylcyclopropylacrylates can be explained by steric effects on the formation of a single conjugated system and linked with the relative orientation and the degree of overlap of the orbitals of the three-membered ring with the π-orbitals of neighbouring unsaturated groups. Such overlapping is evidently weaker in the *cis*-isomers, which is probably responsible for the hypsochromic displacement of the longer-wavelength absorption band and its diminished intensity in comparison with the *trans*-isomers[217].

In contrast to earlier results[218] indicating absence of appreciable conjugation between a cyclopropyl ring and substituents (study of the electronic and circular dichroism spectra of *trans*-2-phenylcyclopropanecarboxylic acid), a subsequent careful investigation[219] of the ultraviolet and circular dichroism spectra of the same acid has revealed the presence of some electronic interaction between phenyl and carboxyl chromophores and the transmission of electronic effects through the cyclopropane ring.

Steric conditions necessary for maximum delocalisation of electrons in a system comprising cyclopropyl and an unsaturated group in an excited state were postulated by several workers[170,184,185,207,213,220]: (i) the π-bonds of the unsaturated group and the cyclopropane ring should be coplanar; and (ii) the plane containing the atoms of the unsaturated group should cut the three-membered ring along a bisecting line. However, study of conjugation effects in phenylcyclopropane derivatives with a fixed spatial arrangement of the phenyl group and the cyclopropane ring led to the conclusion that no preferred geometry exists for conjugation between them[209]. Examination of the electronic spectra of many cyclopropyl ketones indicated also considerable conjugation interaction between the three-membered ring and the unsaturated centre even when only one cyclic carbon–carbon bond was involved in conjugation[205]. Thus conjugation and the transmission of electronic effects through a cyclopropane ring in the excited state constitute an extremely complicated problem.

Table 6. Reaction constants ρ for $R.C_6H_4.X.COOC_2H_5$ (correlation analysis of alkaline hydrolysis constants).

X	ρ	X	ρ
$-CH_2-CH_2-$	0.591		0.812
trans-CH=CH-	1.314		
cis-CH=CH-	1.122		1.02

Relatively little study has been made of the transmission of the effect of substituents through the cyclopropane ring in a reactive state. Thus correlation analysis of the alkaline hydrolysis constants of ethyl *meta*- and *para*-substituted *trans*- and *cis*-2-phenylcyclopropanecarboxylates in 87.8% ethanol at 37°C enabled reaction constants to be determined for these series (Table 6) and the ability to transmit electronic effects in comparison with *cis*- and *trans*-cinnamic, β-phenylpropionic, and phenylpropiolic esters to be assessed as lying in the sequence[221]

$$CH_2.CH_2 < \textit{trans}\text{-}\Delta < \textit{cis}\text{-}\Delta < \textit{cis}\text{-}CH:CH < \textit{trans}\text{-}CH:CH < C:C.$$

Measurements of ionisation constants were used to assess the effect of two phenyl groups separated by a three-membered ring in 2,3-diphenylcyclopropanecarboxylic acids[222].

Correlation analysis of a kinetic study of the reaction of diphenyldiazomethane with *trans*-2-arylcyclopropanecarboxylic acids in toluene at 35–65°C established that use of the σ-constants of substituents in the aromatic ring gives the best correlation of the esterification rate constants. The transmission factor π' for the three-carbon ring was also calculated[223]. The result (0.40) was close to the value π' = 0.33 calculated from the p*K* of cyclopropanecarboxylic acids[224]. The data indicate that the effect of the aryl group is transmitted to the carboxyl mainly by an inductive mechanism.

Correlation analysis of the half-wave reduction potentials of compounds $R.C_6H_4.X.CO.C_6H_5$ (where X represents vinylene, cyclopropylene, or a single bond) in acid medium (pH 2.4 in 50% dimethylformamide) revealed that the best results are obtained by using the Hammett σ-constants and the Taft σ^0-constants. Values of ρ (in mV) corresponding to the above bridges X were −130 (σ), −272 (σ and σ^0), and −339 (σ).[225] Since benzophenones (standard series) and cyclopropyl ketones had different mechanisms of reduction, however, the transmission factor π' unfortunately could not be calculated. The observed correlation of half-wave potentials with the σ^0-constants indicates the important part played by inductive effects in the series of cyclopropyl ketones studied.

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