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# Chemistry of methylenecyclobutane

M G Vinogradov, A V Zinenkov

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**Abstract. Studies devoted to the synthesis, investigation of the properties, and chemical transformations of methylenecyclobutane are surveyed systematically. Data on the reactions of methylenecyclobutane with a broad range of reagents are presented. The bibliography includes 291 references.**

## I. Introduction

Methylenecyclobutane (MCB) is a side product in the production of isoprene by the catalytic cleavage of 4,4-dimethyl-1,3-dioxane,[1,2] which makes it a potential raw material for fine organic synthesis. Due to the presence of two reactive groups, the double bond, and the cyclobutane ring in its molecule, methylenecyclobutane can undergo a variety of chemical transformations, which permits the use of this compound in small-scale chemistry (for example, in the production of pesticides, pheromones, medicinals, and perfumes).

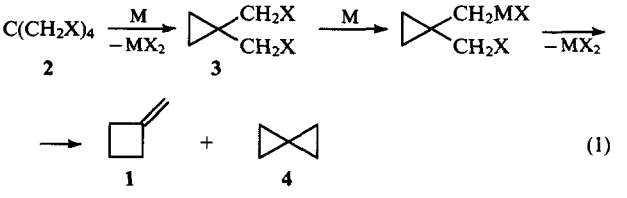
At present, MCB is not produced as a commercial target product in any large quantities. However, it is available as a reagent. For example, 'Aldrich' offers a preparation with a MCB content not less than 92%, and 'EGA-Chemie' supplies methylenecyclobutane of > 97% purity (the remaining 3% is due to spiropentane).

### 1. Preparation

Methylenecyclobutane **1** was first obtained by Gustavson[3,4] in 1896 by the treatment of 2,2-di(bromomethyl)-1,3-dibromopropane [tetrabromoneopentane **2**, (X = Br)] with zinc dust in ethanol (the Gustavson method[5]). Gustavson intended to obtain spiropentane **4**, but the resulting hydrocarbon differed in its properties from spiropentane. He studied this compound and mistakenly attributed the structure of vinylcyclopropane to it.

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(1)

To determine the structure of this hydrocarbon proved fairly difficult. The problem of the structure of the 'Gustavson's hydrocarbon' was ultimately solved as late as 1914 by Filipov,[6,7] who also presented a detailed list of the papers dealing with the synthesis and properties of MCB published up to that time. The data on the debromination of tetrabromoneopentane published before 1944 are presented in a review.[8]

In subsequent years, researchers paid considerable attention to the reaction of tetrabromoneopentane with zinc.[9–16] It has been shown that isomerisation occurs during the elimination of the second pair of bromine atoms from the intermediate 1,1-di(bromomethyl)cyclopropane **3**. When $Zn^{2+}$ cations, which catalyse the rearrangement of **3**, are bound into an inactive complex, spirocyclopentane **4** is formed predominantly.[12] The influence of the nature of the halogen atom and the solvent on the reaction of tetrahaloneopentanes **2** with zinc has been studied.[13–16]

Further studies[17–20] have shown that the ratio between spiropentane and methylenecyclobutane depends on the nature of the metal used as the reducing agent and the acidity of the medium.

The preparative synthesis of MCB by the reduction of tetrabromoneopentane with zinc dust[21] is most frequently mentioned in the literature.

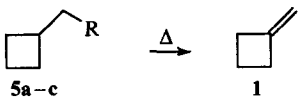
It has been suggested that tribromoneopentyl benzenesulfonate, which is more readily available than tetrabromoneopentane, be used in the synthesis of MCB.[22]

Methylenecyclobutane is formed, apart from other hydrocarbons, on reduction of trihalo-derivatives of neopentane.[23,24]

Dehydration of 1-methylcyclobutanol gave a mixture of hydrocarbons consisting of 1-methylcyclobutene (~45%), isoprene (~35%), and MCB (~20%) in a low yield.[25]

The pyrolysis of cyclobutylmethyl acetate **5a** at 480 °C leads to MCB in 70% yield, and the pyrolysis of the corresponding

*S*-methyl xanthate **5b** at 380 °C affords MCB in 65% yield.[26] In the thermolysis of dimethyl(cyclobutylmethyl)amine oxide **5c**, the yield of MCB reaches 95%.[27]



**5a–c** **1**

R = OAc (**a**), $OCS_2Me$ (**b**), $NOMe_2$ (**c**)

Methylenecyclobutane can also be synthesised starting from 1,4-dibromobutane via cyclobutylidenetriphenylphosphorane[28] or by the thermal,[29] mercury-photosensitised,[30] or laser-induced[31] isomerisation of spiropentane, but these reactions can hardly be regarded as preparative methods for synthesising MCB.

In the industrial production of isoprene from isobutene and formaldehyde by the Prins reaction,[5] the still product in the column for the purification of isoprene has been found to contain some MCB.[1,32] A method for the isolation of MCB from this mixture by fractionation has been suggested.[2] The specimen thus obtained contained 98.42% of MCB. To identify MCB in the fractions of $C_5$ hydrocarbons, gas chromatograhy–mass spectrometry (GCMS) has been used.[33] The liquid–vapour phase equilibria in the systems obtained in the production of isoprene and containing MCB and other hydrocarbons have been considered in a number of papers.[34–37]

## 2. Structure and physical properties of methylenecyclobutane

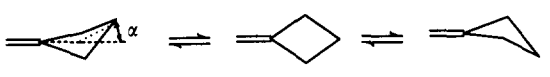
At present, numerous data on the geometric structure of MCB are available. In fact, NMR,[38–49] IR,[49–54] UV,[49,55] photoelectron,[56–58] mass,[59–64] microwave,[65–67] and Raman,[13–16,68–70] spectra of MCB have been studied in detail. Its physical and thermodynamic characteristics have been determined.[59,71–76]

Numerous theoretical studies have been devoted to the problems of the geometry and energetics of the MCB molecule.[50,58,77–100] The authors of these studies used various quantum-chemical computational methods.

According to the computational and experimental data, the MCB molecule possesses conformational mobility. The energy barrier to the transition from the puckered to the planar conformation is fairly low (−0.2 kcal $mol^{-1}$); it is lower than that for unsubstituted cyclobutane by a factor of 4–5. This distinction is due to the lesser changes in both the angular strain and the torsional interactions which accompany the transition of MCB from the nonplanar to the planar configuration.[98]

Unambiguous data concerning the value of the dihedral angle (α) in the puckered conformation (Scheme 1) are lacking. For example, a dihedral angle of 16° has been found from spin–spin coupling constants.[48] It follows from electron diffraction, microwave spectra, and quantum-chemical calculations that the angle is 21.6°,[100] which is lower than for unsubstituted cyclobutane, in which the angle α is 30°[101,102] or 25°.[100]

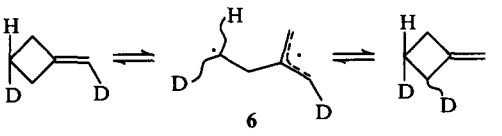
Scheme 1



The C=C bond length in MCB is 1.331 Å.[91] It differs little from the length of the double bond in isobutene (1.330 Å) and is shorter than this bond in ethene (1.337 Å).[90]

# II. Rearrangements

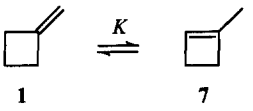
Whereas at ambient or low temperature MCB undergoes only conformational transformations (Scheme 1), at elevated temperatures (300–350 °C) a reversible process involving a more extensive structural rearrangement of the C–C and C–H bonds is observed. Thus, at a temperature of 332 °C partially deuteriated MCB undergoes a redistribution of deuterium atoms, which is due to the relative ease of the homolytic cleavage of C–C bonds in the strained four-membered ring, yielding the alkylallyl biradical **6**.[103]



**6** (2)

The isomerisation of MCB via a biradical mechanism has been discussed in another study.[104] A quantum-mechanical calculation carried out more recently also provided evidence in support of this mechanism of the thermal rearrangement of MCB.[105]

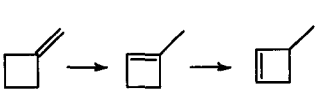
The rearrangement of MCB involving the *exo–endo* migration of the double bond to give 1-methylcyclobutene **7** is of considerable interest.



**1** **7** (3)

Like MCB, the latter compound is potentially likely to be useful in organic synthesis. The rearrangement of MCB is energetically the least favourable compared with the corresponding rearrangements of its homologues with larger rings, since the $\Delta H$ value for this reaction is fairly small (−0.54[106] and −0.9 kcal $mol^{-1}$ [107]). For the rearrangements of methylenecyclopentane and methylenecyclohexane, these values are −3.65 and −1.97 kcal $mol^{-1}$, respectively.[108]

MCB rearranges to 1-methylcyclobutene when it is passed over $Al_2O_3$ at 300 °C,[6] but, isomerisation under these conditions can also yield isoprene.[109] When MCB is passed over $Al_2O_3$ at a higher temperature (370–420 °C),[110] the ring is cleaved to give isoprene as the main reaction product.[109,110] The isomerisation of MCB on passing it over various heterogeneous catalysts (aluminosilicates or zeolites) in the temperature ranges 50–400 °C[111] and 350–500 °C[112] has been described. For all the catalysts studied, it was found that the curves for the temperature dependence of the yield of 1-methylcyclobutene pass through a maximum. When the temperature is increased further, migration of the double bond within the four-membered ring occurs, yielding 3-methylcyclobutene **8**.[111] This compound is the least stable among the three isomers **1**, **7**, and **8**.[109] Isomer **8** was not detected in the products of the isomerisation of MCB over $Al_2O_3$.[108]



**1** **7** **8** (4)

It has been shown[6] that MCB isomerises to 1-methylcyclobutene when heated in aqueous alcohol in the presence of $ZnBr_2$ and Zn(OH)Br at 140 °C for several days.

Heating of MCB in dimethylacetamide for 10 min at 160 °C gave an equimolar mixture of MCB and 1-methylcyclobutene in 80% yield.[113]

When MCB is stirred at room temperature with metallic sodium deposited onto $Al_2O_3$, an equilibrium between the alkenes with the *exo-* and *endo*-arrangements of the double bond is established after several hours. The equilibrium constant $K$ of reaction (3) at 20 °C is equal to 6, which implies that the reaction mixture contains 15% of MCB and 85% of 1-methylcyclobutene.[109,114–117] As shown in another study,[118] this process is not selective, since after its completion the reaction mixture contains 75% of 1-methylcyclobutene, 19% of MCB, 3% of spiropentane, and 3% of unidentified hydrocarbons.

The isomerisation of MCB also takes place in the presence of strong bases. The relative rates of formation of carbanions from

$C_4-C_8$ methylenecycloalkanes in the presence of potassium *tert*-butoxide in dimethyl sulfoxide have been reported.[119] Kinetic studies of the isomerisation of MCB in the presence of potassium or lithium *tert*-butoxide in various solvents have been carried out.[120] A preparative procedure for the isomerisation of MCB to 1-methylcyclobutene in the $Bu^tOK-DMSO$ catalytic system has been reported;[121] however, the yield of compound **7** per unit volume of the catalyst solution did not exceed 0.1 g $cm^{-3}$ $h^{-1}$. In the presence of a stronger base, lithium β-aminoethylamide, in ethylenediamine at 10–45 °C, the isomerisation proceeds more effectively (with a productivity of 4.3–4.5 g $cm^{-3}$ $h^{-1}$). The equilibrium concentrations of MCB and 1-methylcyclobutene (84%–87% MCB[122]) are virtually attained over a period of several hours.

The isomerisation of MCB [reaction (3)] in the presence of 3 mol % the rhodium hydride complex $Rh(H)(CO)(PPh_3)_3$ (with benzene as the solvent)[123] occurs much less effectively: even after 10 days the composition of the reaction mixture is far from equilibrium (the ratio between isomers **1** and **7** is 0.68 instead of 0.17). In all probability, the reaction proceeds via a π-complex of Rh(I) with MCB (see below). The isomerisation of MCB to 1-methylcyclobutene has also been observed in the presence of $PdCl_2$ at 100 °C in dioxane and at 22 °C in methanol.[124,125]

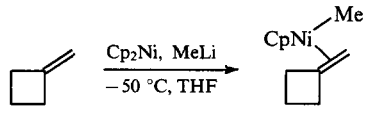
## III. Formation of complexes with metals

Like other alkenes, MCB forms complexes with $AgNO_3$. The stability constants of some complexes of alkenes determined by GLC have been reported.[126,127] The formation of complexes with Ag(I) has been used in the analysis of MCB-containing mixtures of light hydrocarbons.[128]

Methylenecyclobutane reacts with Pd(II) chloride or $[Rh(CO)_2Cl]_2$ to give π-allylic complexes.[129]

The comparative stabilities of Rh(I) complexes with various alkenes have been studied.[130] The π-complex derived from MCB was found to possess an anomalously high stability, comparable with that of the Rh(I) complex of ethene.

The synthesis of a π-complex of MCB with Ni(II) (yield 61%) has also been reported.[131]




**9**

A trinuclear cluster-type osmium complex incorporating MCB has been described.[132] In this complex, MCB forms a bridge between two osmium atoms via the methylidene carbon atom and also forms a π-bond with the third osmium atom.

The interaction of MCB with organotitanium,[133] organonickel,[134] organorhodium,[135] and organopalladium[136] compounds has also been described in the literature.

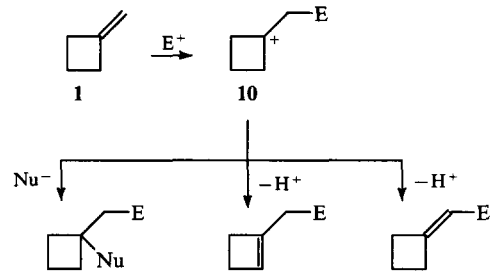
## IV. Addition to the exocyclic double bond without formation of new C–C bonds

### 1. Reactivity

#### a. Cationoid intermediates

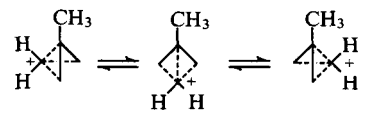
Many known transformations of MCB involve a stage in which active electrophilic species such as protons, acylium cations, etc. add to the double bond. The addition results in the tertiary carbocationic intermediate **10**, which can either combine with a nucleophile or eliminate a proton, and this governs the composition of the final reaction products (Scheme 2).

Scheme 2

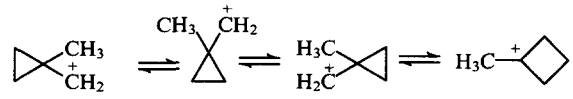



The problem of the structure of the intermediate cation **10** (E = H) has attracted considerable attention and has not yet been solved. According to $^{13}C$ NMR spectroscopy and an isotope study, at −154 °C this cation exists as the symmetrical σ-bridged methylcyclobutanium structure **11**,[137,138] while from −150 to −90 °C it is an equilibrium mixture of three bicyclobutanium ions **11**, **12a**, and **12b** or delocalised 1-methylcyclopropylcarbynyl cations **13a–c** interconverting via the classical planar 1-methylcyclobutyl cation **14** (Scheme 3).

Scheme 3



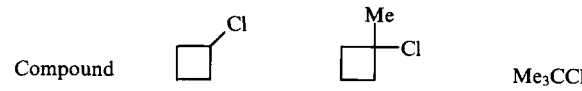

**12a** **11** **12b**




**13a** **13b** **13c** **14**

The conformation of the 1-methylcyclobutyl cation **10** (E = H) in an aqueous medium at ambient temperature is unknown. Quantum-chemical calculations referring to the gaseous phase allow the existence of this cation as any of the above structures or as their equilibrium mixture.[139–141] At the same time, since the tertiary carbocation **14** must be much more stable than the primary rearranged cations **13a–c**, one should expect that the equilibrium would be substantially shifted to the right, that is, toward the formation of the cation **14** (Scheme 3). Therefore, it is the transformations of the nonrearranged cation **10** (Scheme 2) that should determine the composition of the products of electrophilic addition to the double bond of MCB; this is in good agreement with the existing experimental data.

The relative stability of the cation **10** (E = H) can be judged by comparing the rate constants for the solvolysis of the corresponding chlorides **15–17** (80% acetone, 25 °C).[142]

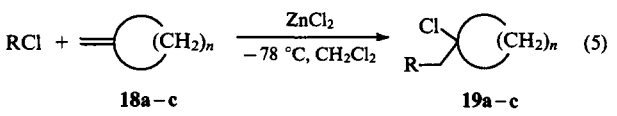



**15** **16** **17**

| | | | |
|---|---|---|---|
| $k/s^{-1}$ | $1.81 \times 10^{-9}$ | $1.15 \times 10^{-7}$ | $1.97 \times 10^{-6}$ |

The above data indicate that the cation **10** (E = H) is more stable than the unsubstituted cyclobutyl cation and is less stable than the *tert*-butyl cation.

The reactivity of MCB toward electrophilic addition can be estimated by comparing the rates of the $ZnCl_2$-catalysed reaction of $(p\text{-}CH_3C_6H_4)_2CHCl$ with various methylenecycloalkanes **18a–c**.[143]




**18a–c** **19a–c**

R = (*p*-$CH_3C_6H_4$)$_2$CH

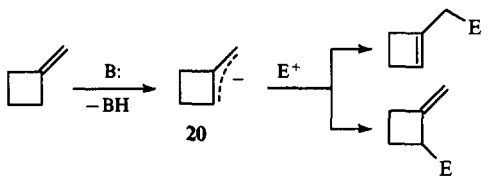
| *n* | 3 | 4 | 5 |
|---|---|---|---|
| *k* (arbitrary units) | 1 | 51.1 | 1.03 |

It follows from these data that the reactivity of MCB in reaction (5) with the above electrophile is close to that of methylenecyclohexane, but is many times lower than that of methylenecyclopentane.

**b. Anionoid intermediates**

Another important aspect of using MCB in organic synthesis is based on its deprotonation through the action of a strong base and the subsequent transformations of the allylic carbanion **20** thus generated (Scheme 4).

Scheme 4

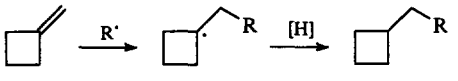



**20**

The composition of the products of transformation of the carbanion **20** is determined by the direction of attack by the electrophile ($E^+$), which is either on a carbon atom of the side chain or on a ring carbon atom in the allylic system. The predominance of either of these directions depends on the nature of the electrophile and on the conditions under which the reaction is carried out.[144]

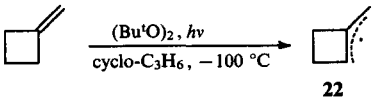
**c. Free-radical intermediates**

Another approach to the functionalisation of MCB is based on the radical addition to the double bond. The intermediate adduct formed in this reaction (radical **21**), like the corresponding carbocation **10** produced in the electrophilic addition to MCB (see above), does not undergo fragmentation, and the cyclobutane ring is retained in the products of its transformation.




**21**

The radicals **21**, in which R = $SiMe_3$, $SiEt_3$,[145,146] or MeS,[147] have been detected by EPR at 150–220 K. The formation of the allylic radical **22** upon photolysis of a solution of MCB in cyclopropane containing di-*tert*-butyl peroxide has also been detected by EPR.[148]

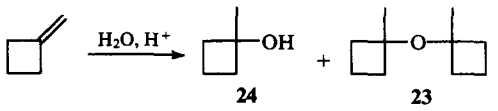



**22**

Radical-ion species such as radical cations can also participate in reactions with MCB. The latter are formed, for example, in photoinduced[149] or γ-radiation-induced reactions.[150]

## 2. Addition with formation of the C–O bond

The acid-catalysed hydration of MCB is among the thoroughly studied examples of electrophilic addition to the double bond of MCB.[151–154] The mechanism of this reaction has been described by Taft,[155] who has also determined its thermodynamic parameters.[156] The ether **23**, resulting from the addition of 1-methylcyclobutanol **24** to MCB, is formed in this reaction as a side product.

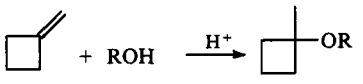



**24** **23**

When MCB was hydrated in the presence of the KU-23(10/60) cation-exchange resin at 40 °C with an MCB : $H_2O$ molar ratio of 2 : 3 and a reaction time of 8 h, the degree of MCB conversion amounted to 87.8% and the selectivity of the formation of compound **24** was 94.4% (the reaction mixture contained 3% of the ether **23**). However, by varying the hydration conditions one can direct the process to the selective formation of the ether **23**. Thus, at 40 °C, for an MCB : $H_2O$ molar ratio of 2 : 1, and for a reaction time of 3 h, the selectivity of the formation of ether **23** was 96%, the degree of conversion of MCB being 92.1%.[152]

The hydration of MCB under static conditions (without stirring) in the presence of the KU-23(10/60) cation-exchange resin in a batch reactor has been described.[153]

Alcohols or carboxylic acids add to MCB in the presence of an acid catalyst.[157]




**25**

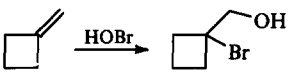
| R | Me | Et | Bu$^n$ |  | MeCO |
|---|---|---|---|---|---|
| Yield (%) | 90 | 45 | 41 | 63 | 56 |

| R | $ClCH_2CO$ | $FCH_2CO$ | $Cl_2CHCO$ | $CF_3$ |
|---|---|---|---|---|
| Yield (%) | 55 | 60 | 90 | 91 |

The reaction is carried out in hexane with MCB : ROH (or RCOOH) : $C_6H_{14}$ ratios of 1 : 1 : 1 in the presence of sulfuric acid or HCl.

Esters derived from 1-methylcyclobutanol have found application as insecticides, acaricides, and fungicides,[158,159] and sugar substitutes in foodstuffs.[160] The 1-methylcyclobutoxy-group is incorporated in a metabolism-resistant β-lactam antibiotic possessing a high antibacterial activity.[161]

The selective addition of HOBr to MCB, affording 1-bromo-1-hydroxymethylcyclobutane in 78% yield, has been described.[162,163]



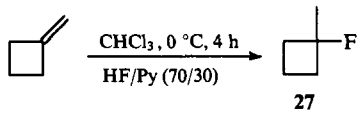

**26**

Hypochlorous acid also adds to MCB, but, apart from chlorohydrin, this reaction yields a diol (the ratio between these products is 3 : 2).[162] The process is carried out in an aqueous suspension of the alkene.

## 3. Addition with formation of the C–N, C–S, C–Se, or C–Hal bond

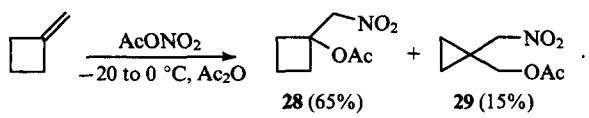
The addition of hydrogen halides to MCB has been studied in detail.[164–168] In polar solvents, hydrogen halides add in conformity with the Markovnikov rule, giving 1-halo-1-methylcyclobutane, while in the presence of a radical source in a nonpolar solvent, anti-Markovnikov addition occurs to yield bromomethylcyclobutane.[162,169,170]

Hittich et al.[171] have described the hydrofluorination of MCB, but the yield of 1-fluoro-1-methylcyclobutane **27** isolated by preparative GLC was not reported.




**27**

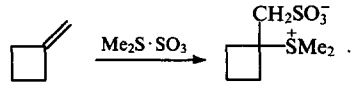
Acetyl nitrate adds to MCB at −20 to 0 °C in the presence of acetic anhydride.[172] Apart from the major product, 1-acetoxy-1-nitromethylcyclobutane **28**, the reaction yields the product **29** of the rearrangement of the intermediate cation involving ring contraction:




**28** (65%) **29** (15%)

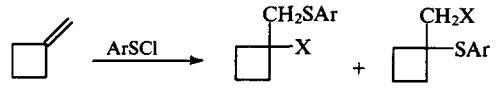
When $NO_2BF_4$ is used instead of $AcONO_2$, the yield of 1,1-disubstituted cyclopropane is twice as high.[172]

The interaction of MCB with the complex $Me_2S \cdot SO_3$ affords the sulfobetaine **30** as the only product in a high yield:[173,174]




**30**

2,4-Dinitrophenylsulfanyl chloride reacts with MCB in acetic acid at 20 °C to afford predominantly the arylthiomethyl-substituted cyclobutane **31**. In addition, a small amount of compound **32** was isolated (the **31a** : **32a** ratio was 5.2 : 1); the overall yield of the products **31** and **32** was 88%.[175] At 40 °C, these products are formed in a different ratio (**31a** : **32a** = 2 : 1):[176]

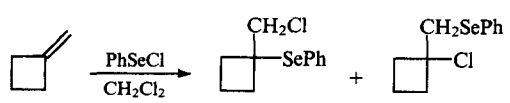



**31a,b** **32a,b**

Ar = 2,4-$(NO_2)_2C_6H_3$; X = Cl (**a**), OAc (**b**).

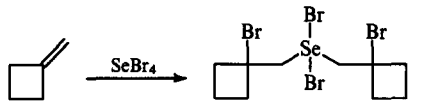
When the reaction is carried out in chloroform, the anti-Markovnikov addition product predominates (**31a** : **32a** = 0.4 : 1),[176] while the process carried out in acetic acid in the presence of $LiClO_4$ affords mostly products of the interaction with the solvent (the products **31** and **32** are formed in the following yields: **31a**, 5%; **31b**, 35%; **32a**, 1%, **32b**, 12%).[176]

Phenylselanyl chloride interacts with MCB at −70 °C in $CH_2Cl_2$ to give the chloromethyl derivative of cyclobutane **33** as the major product; at room temperature, compound **33** slowly isomerises to the chloride **34**.[177]




**33** **34**

The reaction of MCB with $SeBr_4$ gives the product **35** incorporating two cyclobutyl groups:[178]

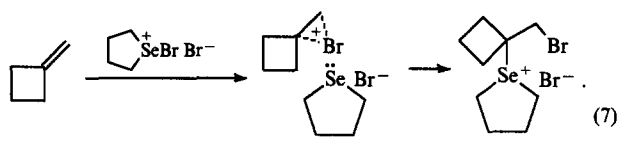



(6)

**35** (43%)

At room temperature, compound **35** is gradually dehalogenated and rearranges, affording substituted cyclopropylmethyl bromides.

The electrophilic addition of tetramethyleneselanyl bromide to MCB gives the selenonium salt **36**.[179] In all probability, this reaction occurs via the intermediate bromonium ion **37**:[180]



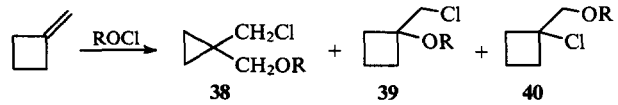

(7)

**37** **36** (90%)

The formation of different products in these reactions (compounds **35** and **36**) may be due to greater steric hindrance in the selenium-containing nucleophile participating in reaction (7), which hampers the attack on the nonterminal carbon atom of the bridged cation **37**.[180]

At −60 °C, MCB can combine with $SO_3$, giving the cyclic β-sultone.[181]

The chlorosulfamination of MCB yields a mixture of the products **38**–**40**. The addition is nonselective and is accompanied by partial rearrangement:[182]




**38** **39** **40**

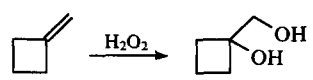
R = $R'_2NSO_2$.

## 4. Hydrogenation

Hydrogenation under mild conditions involves the addition of hydrogen to the exocyclic double bond. Under more drastic conditions, the cyclobutane ring is cleaved and the reaction yields isopentane as the major product.[6] The heats of hydrogenation of MCB and 1-methylcyclobutene have been reported by Turner et al.[107] The kinetics of the hydrogenation of MCB over platinum-containing catalysts have been studied.[183,184]

## 5. Oxidation

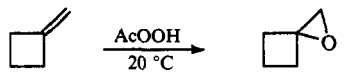
When MCB is treated with hydrogen peroxide in the presence of $OsO_4$ or in formic acid, 1-hydroxy-1-hydroxymethylcyclobutane **41** is formed in 39% and 83% yield, respectively.[21]




**41**

The highly selective dihydroxylation of MCB with hydrogen peroxide occurs in the presence of the osmium catalyst obtained from $OsO_4$ or $Os_3(CO)_{12}$ and poly(4-vinylpyridine) or poly(4-vinylpyridine 1-oxide).[185]

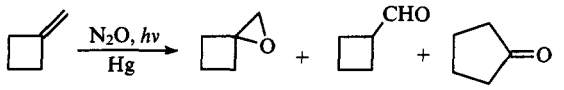
The epoxidation of MCB with 41% peracetic acid in $CH_2Cl_2$ in the presence of anhydrous $Na_2CO_3$ at room temperature gives the oxaspirohexane **42** in 45% yield.[186,187]




42

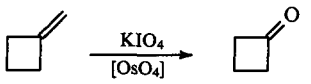
The treatment of MCB with peracetic acid in acetic acid results in a mixture consisting of the monoacetate of the diol **41** and cyclobutanecarboxylic acid, while the use of perbenzoic acid in chloroform yields a mixture of the oxaspirohexane **42** and the monobenzoate of the diol **41**.[188]

The kinetics of the epoxidation of MCB with peroxylauric acid have been studied.[189] The epoxidation of MCB with atomic oxygen, generated by the Hg-sensitised photolysis of $N_2O$, occurs nonselectively: apart from the epoxide **42**, formylcyclobutane **43** and cyclopentanone **44** are produced.[190]




**42** (35%) **43** (29%) **44** (7%)

The oxidative cleavage of MCB by potassium periodate in the presence of a catalytic amount of $OsO_4$ is the simplest of the known ways of preparing cyclobutanone **45**.[191,192]

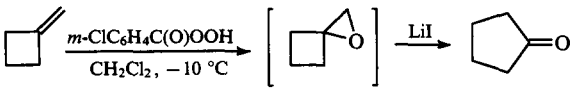



45

Methylenecyclobutane is ozonised at a temperature of −70 °C in pentane. The resulting ozonide decomposes explosively at −20 °C.[193]

Cyclobutanone has been synthesised in a yield of about 70% by the ozonisation of MCB at −70 to −80 °C in $CH_2Cl_2$ in the presence of pyridine.[194,195]

A series of MCB transformations accompanied by ring expansion and resulting finally in cyclopentanone have been described. For example, the oxidation of MCB with nitrous oxide at 300 °C and 450 atm affords cyclopentanone **44** in a low yield.[196] One of these processes involves the intermediate formation of the epoxide **42**, which is then allowed to react with LiI without isolation from the reaction mixture.[197,198]

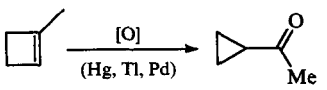



42 **44** (60%)

Methylenecyclobutane can be directly converted into cyclopentanone by oxidation with oxygen in the presence of the $PdCl_2-CuCl_2$ catalytic system. The selectivity of this process depends substantially on the nature of the solvent. It occurs most selectively in benzene, the yield of cyclopentanone being 75%.[199]

The oxidation of MCB to cyclopentanone with the complex $(MeCN)_2PdCl(NO_2)$ in $CH_2Cl_2$ has also been studied.[200]

The oxidation of 1-methylcyclobutene with Tl(III) and Hg(II) perchlorates,[201,202] as well as with $PdCl_2$,[201] $PdCl_2L_2$, or $PdCl(NO_2)L_2$ (L = $CD_3CN$)[203] results in cyclopropyl methyl ketone **46**, the chemistry of which has been discussed in a review.[204]

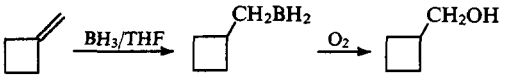



7 **46**

The autooxidation of MCB proceeds more slowly than that of terpenes or other unsaturated alicyclic alkenes, the 2-position of the cyclobutane ring being attacked predominantly.[205]

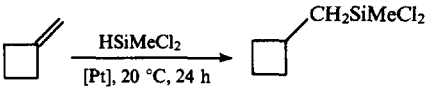
### 6. Hydroboration, hydrosilylation, and hydrophosphorylation

The hydroboration of MCB with the subsequent oxidation of the resulting cyclobutylmethylborane **47** leads to cyclobutylmethanol **48**.[206]



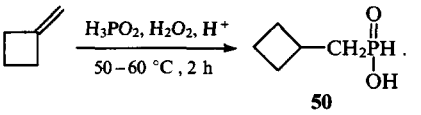

47 **48**

MCB enters into the hydrosilylation reaction in the presence of a Pt catalyst immobilised on a phosphinated silica gel:[207]




49

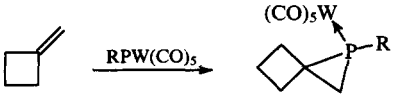
The hydrophosphorylation of MCB with phosphinic acid in the presence of hydrogen peroxide in an acid medium at 50–60 °C affords cyclobutylmethylphosphinic acid **50**:[208]




50

The reaction of MCB with $PBr_3$ gives the corresponding phosphine as the only product.[209] When the reaction is carried out in a stream of $O_2$, the yield of the phosphine increases from 49% to 63%. The reaction is regiospecific and occurs via a radical mechanism.

The treatment of the phosphinidene complexes $PhPW(CO)_5$ and $MePW(CO)_5$ with exocyclic olefins affords 1-phosphaspiro-[2.*n*]alkanes (*n* = 2 – 5).[210] In the case of MCB, a pentacarbonyltungsten complex containing the 1-phosphaspiro[2.3]-hexane ligand **51** is formed.



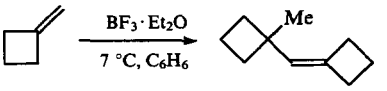

51 a,b

R = Me (**a**), Ph (**b**)

## V. Addition to the double bond with formation of new C–C bonds

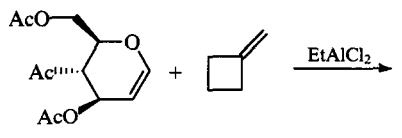
### 1. Alkylation

In the presence of 20 mol % $BF_3 \cdot Et_2O$ in benzene at 7 °C, MCB dimerises, giving the bicyclic dimer **52**.[211]

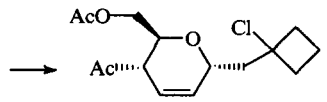



52 (30%)

A new pathway to the synthesis of *C*-glycosides, which are of interest for preparing new anticancer preparations, has been suggested by Herscovici et al.[212,213] This method is based on the electrophilic addition of the acylated glycals **53** to MCB, catalysed by Lewis acids:

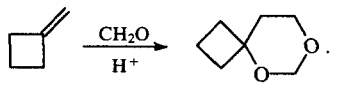


53



54 (80 %) (8)

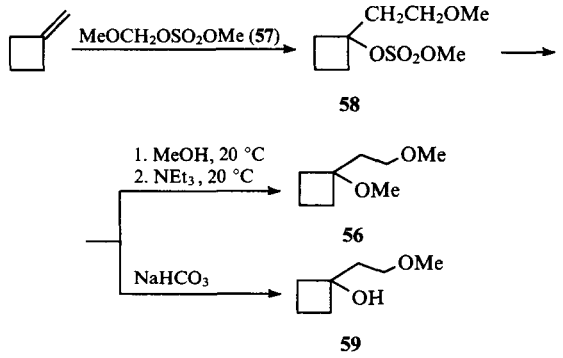
Reaction (8) was carried out at −20 °C for 5 min in a $C_5H_{12}-Et_2O$ (5:1) solvent mixture. A number of workers reported [157,214,215] the preparation of 5,7-dioxaspiro[3.5]nonane **55** by the reaction of MCB with formaldehyde catalysed by sulfuric acid or *p*-toluenesulfonic acid:



55 (49% – 82 %)

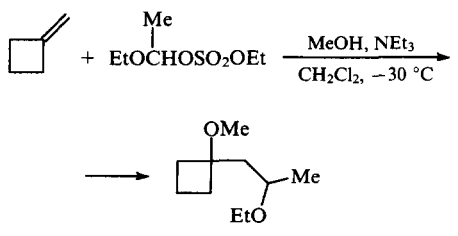
If the above reaction is carried out at 40 °C in the presence of 30 mass % $H_2SO_4$, the yield of compound **55** is 49%.[157,214] The yield of 5,7-dioxaspiro[3.5]nonane can be brought to 82% with virtually complete conversion of MCB by conducting this reaction at 90 °C and with a $CH_2O$:MCB molar ratio of 2:1 in the presence of 2.5 mol % sulfuric acid and an equal volume of an extractant (hexane).[215]

The methylated diol **56** has been obtained directly from MCB using methoxymethyl methyl sulfate **57** as the alkylating reagent.[216]



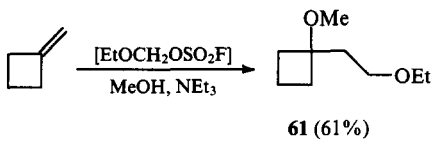
This reaction involves the intermediate formation of the sulfate **58**, which is subjected to methanolysis and then treated with triethylamine without isolation from the solution. When the intermediate **58** is treated with an aqueous solution of $NaHCO_3$, the reaction yields the alcohol **59**.[217]

Similarly, 1-ethoxyethyl ethyl sulfate adds to MCB in the presence of methanol to give the adduct **60**.[218]



60 (25%)

1-(2-Ethoxyethyl)-1-methoxycyclobutane **61** has been synthesised in a similar way.[219]



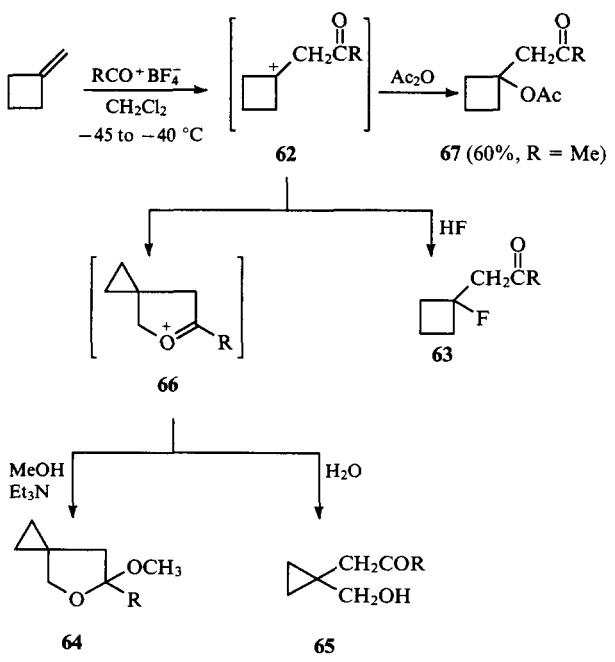
61 (61%)

## 2. Acylation

### a. Electrophilic acylation

The known instances of the electrophilic acylation of MCB involved the highly reactive cationoid reagents $RCO^+X^-$ ($X^- = SO_3F^-$, $BF_4^-$, or $SbF_6^-$) as electrophiles. The course of the reactions of MCB with acyl tetrafluoroborates $RCO^+BF_4^-$ (Scheme 5) depends on the nature of the group R. The bulkier the group R, the larger the contribution of reactions occurring with the rearrangement of the intermediate cation **62**.[220] If R is Me or Et, only the fluorinated ketone **63** is obtained. If R is $Bu^t$, only the rearranged product, namely, substituted tetrahydrofuran **64**, is formed. When R is $Pr^n$ or $Bu^i$, mixtures of the products **63** and **64** are isolated. When water is added to the reaction mixture, the hydroxyketone **65** is produced via the hydration of the rearranged cation **66**.[220]

Scheme 5



(R = $Bu^t$, 65% – 70%)

| R | **63**:**64** ratio |
|---|---|
| Me | 100:0 |
| Et | 100:0 |
| $Pr^n$ | (85–75):(15–25) |
| $Bu^i$ | (30–35):(70–65) |
| $Bu^t$ | 0:100 |

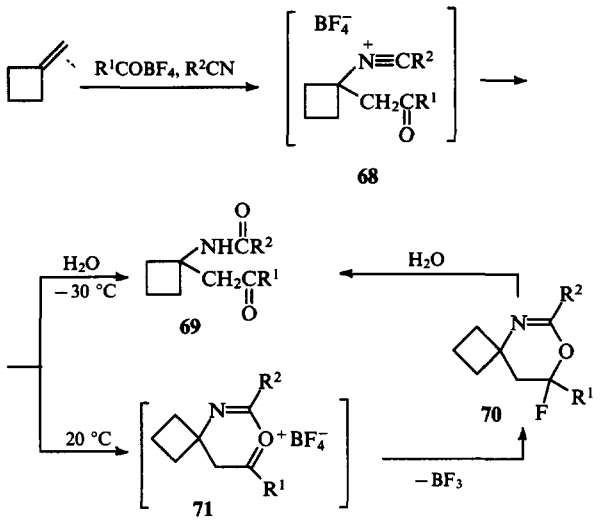
The composition of the products of the acylation of MCB is sensitive not only to the nature of the group R in the cationoid reagent $RCO^+X^-$, but also to the nature of the anion X. The solvent used also plays an important role.

When the acylation of MCB with acetyl tetrafluoroborate is carried out in the presence of acetic anhydride, 1-acetonyl-1-acetoxycyclobutane **67** is the main reaction product (Scheme 5).[221,222]

When $RCO^+BF_4^-$ is replaced by the harder ionic reagent $RCO^+SbF_6^-$, the reaction yields the substituted tetrahydrofuran **64** as the only product, irrespective of the bulk of the group R.[223]

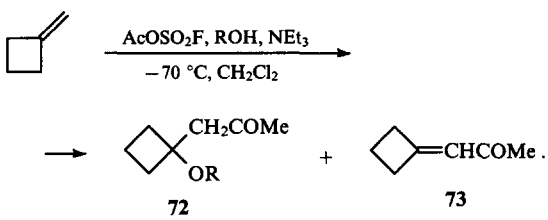
The acylation of MCB with $R^1CO^+BF_4^-$ in the presence of $R^2CN$ proceeds as coupled addition of $R^1CO^+$ and $R^2CN$ to the C=C bond via the formation of the *N*-alkylnitrilium salt **68** (Scheme 6).[222]

Scheme 6



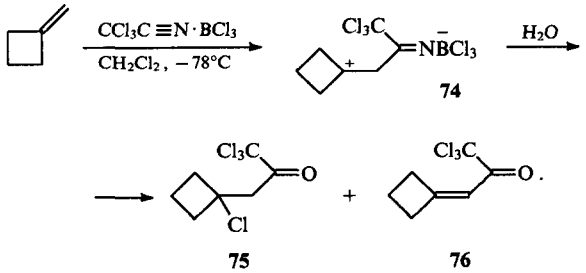
Depending on the reaction temperature, either the amidoketones **69** (−30 °C) or the 5,6-dihydro-1,3-oxazines **70** (+20 °C) are formed selectively. The syntheses of a number of amidoketones **69** and oxazines **70** ($R^1$ = Me, Et, $Pr^n$, $Pr^i$, $Bu^t$; $R^2$ = Me, $CH_2Cl$, Ph) in 34% – 100% yields have been reported by Gridnev et al.[224]

In the case where acetyl fluorosulfonate, prepared in situ from AcF and $SO_3$, is used in the acylation of MCB, the composition of the reaction products depends on the nature of the alcohol introduced into the system:[225]

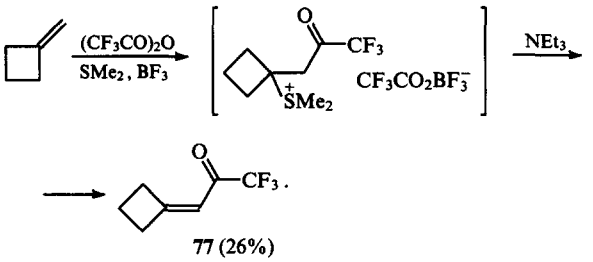


| Alcohol | **72**:**73** ratio | Overall yield (%) |
|---|---|---|
| MeOH | 7:5 | 65 |
| $Pr^nOH$ | 6:1 | 44 |

It has been reported that the complex of trichloroacetonitrile with boron trichloride can be used as a chemical equivalent of the acylium cation.[226] The first step of the process affords the cation **74**, which is converted in the presence of water mostly into the ketone **75** and, to some extent, into the unsaturated ketone **76**. The overall yield of the products is 91%:[226]

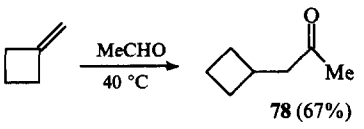


The introduction of a perfluoroacyl group into unsaturated compounds is hampered, because the perfluoroacyl cation is easily decarbonylated and, furthermore, the readily available trifluoroacetic anhydride is insufficiently electrophilic to acylate alkenes. It has been suggested that the perfluoroacylation should be carried out using the complex resulting from the addition of trifluoroacetic anhydride to a solution of dimethyl sulfide in $CH_2Cl_2$ saturated with $BF_3$:[227]



**b. Free-radical acylation**

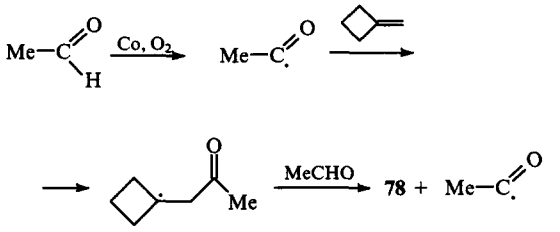
Only one example of the free-radical acylation of MCB is known. It is the reaction of MCB with acetaldehyde (with an AcH : MCB molar ratio of 10 : 1) initiated by atmospheric oxygen (at an air flow rate of 40 $h^{-1}$) in the presence of a catalytic amount of $Co(OAc)_2$ ($1.5 \times 10^{-3}$ mol $l^{-1}$).[228] Apart from the ketone **78**, acetic acid is also formed.



(9)

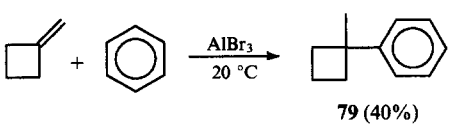
Reaction (9) proceeds by a chain mechanism[229] involving the formation of acyl radicals, their addition to the double bond of MCB, and chain transfer by the intermediate radical adducts:

Scheme 7

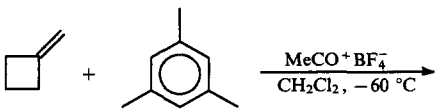


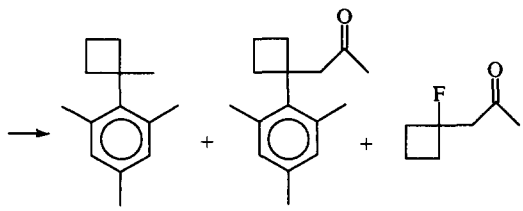
## 3. Arylation

Only a few examples of the arylation of the MCB double bond are known. For example, in the presence of $AlBr_3$, MCB reacts with benzene, yielding 1-methyl-1-phenylcyclobutane **79**:[211,230]



The reaction of MCB with mesitylene in the presence of $MeCO^+BF_4^-$ affords a mixture of arylation (**80**), acylation (**63**), and coupled addition (**81**) products.[231]

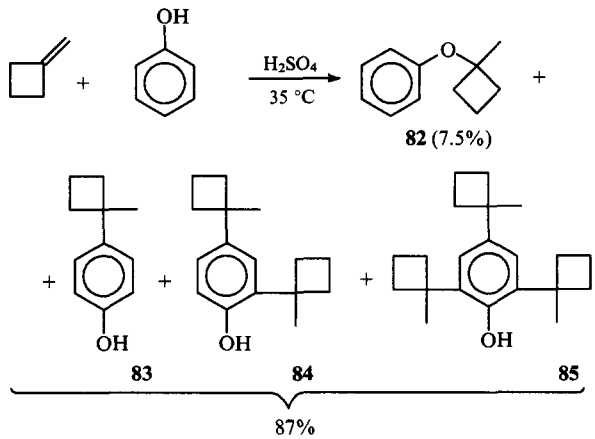




**80** (27%) **81** (3%) **63** (38%)

If this reaction is carried out in the presence of $BF_3$, the yield of compound **80** is only 5%, and in this case extensive polymerisation of MCB is observed.[231]

The reaction of MCB with phenol yields mostly a mixture of mono-, di-, and tri(1-methylcyclobutyl)phenols **83**–**85** and a small amount of the ether **82**.[232]



**82** (7.5%)

**83** **84** **85**

87%

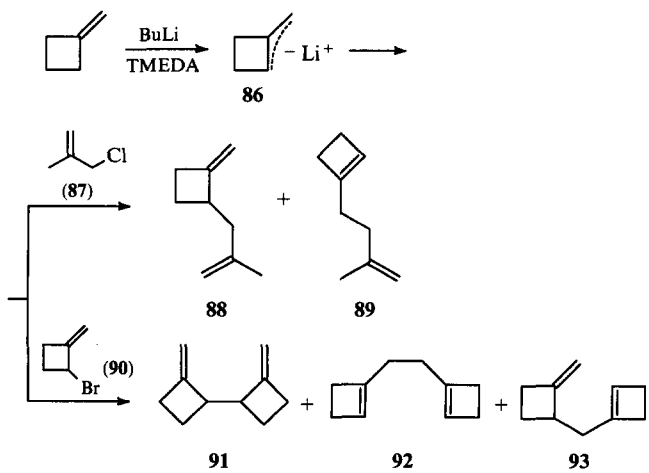
Depending on the reaction conditions, arylation may afford a mono- or disubstituted phenol as the major product (yield 30%–40%).[157]

The reactions of MCB and other methylenecycloalkanes with (*p*-anisyl)phenylcarbenium tetrachloroborate have been studied.[233]

## VI. Reactions with retention of the C = C bond

### 1. Allylic alkylation, 'ene' reactions

The allylic anion **86** prepared from MCB and butyllithium in tetramethylethylenediamine (TMEDA) reacts with methylallyl chloride **87** to give a mixture of the isomers **88** and **89** usual for allylic systems (**88** : **89** = 85 : 15, overall yield 90%).[234]



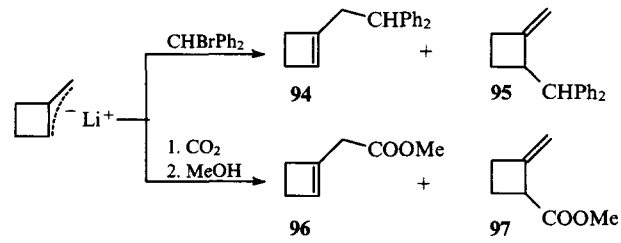
**86**

**88** **89**

**91** **92** **93**

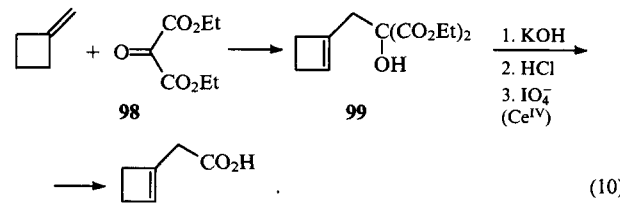
The alkylation of the allylic anion **86** with 2-bromo(methylenecyclobutane) **90** affords a more complex mixture of products, since in this case not only the anion **86**, but also the bromide **90** are capable of reacting at two centres. The product ratios are **91** : **92** : **93** = 22 : 46 : 32, with an overall yield of 85%.

The alkylation of the anion **86** with diphenylmethyl bromide gave compounds **94** and **95** (in a 1 : 1 ratio) in an unexpectedly low yield (17%).[235] The carboxylation of this anion with carbon dioxide proceeds with an equally low yield.[236]



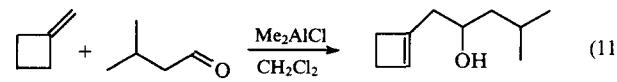
**94** **95** **96** **97**

Carbonyl compounds can also be used as the electrophilic component in the alkylation of MCB.[236–240] Thus, Snider et al.[238] have suggested a method of preparing cyclobutenylmethyl-(hydroxy)malonate from MCB and diethyl oxomalonate **98**. The reaction occurs without a solvent at 80 °C over a period of 170 h. The yield of the alkylation product **99** is 63%. Its hydrolysis followed by oxidation affords 1-cyclobutenylacetic acid **100**:[239]



**98** **99** **100** (96%–98%) (10)

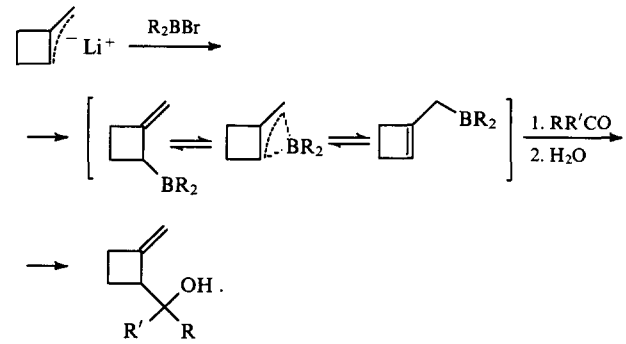
A similar reaction with isovaleraldehyde leads to the alcohol **101** in 43% yield.[238]



**101** (11)

It is noteworthy that the 'ene' reactions (10) and (11) are highly regioselective: in both cases, the addition involves exclusively the *exo*-methylene group of the allylic anion.

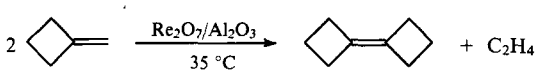
The selective alkylation of MCB with ketones (acetone, cyclohexanone, cycloheptanone, or camphor) at the allylic carbon atom of the cyclobutane ring can be carried out by using the novel approach described by Bubnov et al.[241] A characteristic feature of this approach is that alkylation with an electrophile (in this instance, with a ketone) is preceded by the introduction of a boron-containing group into the allylic anion **86**:



**102** (65%–80%)

### 2. Metathesis (disproportionation) and cometathesis

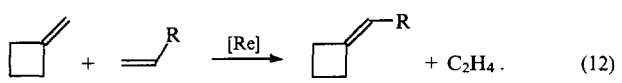
The catalytic disproportionation of MCB in the presence of a heterogeneous rhenium-containing catalyst has been reported in a number of studies carried out mostly in the 1970s.[242-247]




**103**

The yield of bicyclobutylidene **103** in this reaction, carried out in the liquid phase with constant removal of ethene from the reaction zone, reached 70% over a period of 4 h. The disproportionation of MCB can also be carried out in the gaseous phase over the same catalyst in a flow-type setup at 100 °C. The $WCl_6-EtAlCl_2-EtOH$, $WCl_6-Bu^nLi$, and $MoO_3/Al_2O_3$ systems turned out to be virtually inert in this reaction.

Catalytic processes involving the cometathesis of MCB with other alkenes have also been developed:[245,247-249]



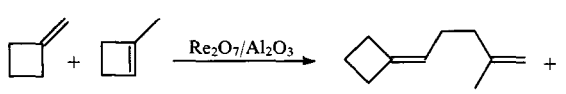

(12)

**104**

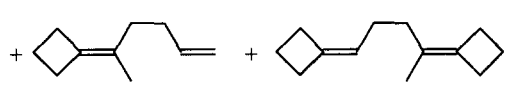
The products of the homometathesis of MCB and $CH_2=CHR$ (which are not shown in the scheme) are also formed in reaction (12).

From a mixture of liquid products of the joint disproportionation of MCB and propene in a flow-type setup in the gaseous phase (with $Re_2O_7/Al_2O_3$ as the catalyst, MCB : propene = 2 : 1, volume rate of supply of the reactants 500 $h^{-1}$, 1 : 1 dilution with nitrogen, 20 °C), ethylidenecyclobutane **104** (R = Me) was isolated in 20% yield.[245]

The cometathesis of MCB with 1-methylcyclobutene affords a mixture of three diene hydrocarbons (**105-107**), the yield of each depending on the reaction conditions (with $Re_2O_7/Al_2O_3$ modified by $SnBu_4$ as the catalyst and benzene as the solvent).[248]

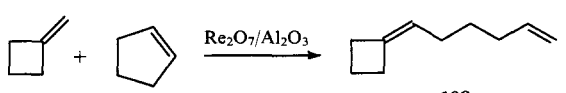



**105**




**106** **107**

The cometathesis of MCB and cyclopentene (CP) was carried out at low initial concentrations of the latter (MCB : CP = 9 : 1) in order to exclude the possibility of its polymerisation, and at temperatures between −65 and 35 °C. At 35 °C, with a CP : catalyst ratio of 10 : 1 by weight, and for a contact time of 1 h, the reaction gave 6-cyclobutylidenehex-1-ene **108** as the only cometathesis product (the degree of conversion of cyclopentene was 90%).[249]

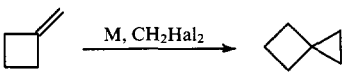



**108**

## VII. Cycloaddition

### 1. [2 + 1]-Cycloaddition

The interaction of MCB with dihalomethanes in the presence of metals such as Zn, Cd, or Cu with a $CH_2Hal_2$ : metal molar ratio of 1 : 2 in a polar solvent (DMF, dimethylacetamide, acetonitrile, *N*-methylpyrrolidone, HMPA, formamide) results in the formation of spirohexane **109**:[250]



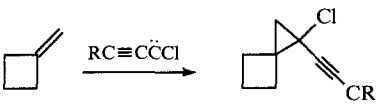

**109**

M = Zn, Cd, Cu .

Spirohexane **109** (yield 48%) has also been obtained by the cyclopropanation of MCB with diazomethane in ether at −10 °C in the presence of palladium acetylacetonate as the catalyst (1 mol% with respect to MCB).[251]

Dichlorocarbene adds to MCB to give 1,1-dichlorospiro[2.3]-hexane.[252]

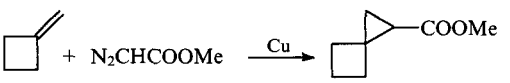
Alkynylhalocarbenes also add to MCB, yielding the corresponding substituted spirohexanes **110**.[253]




**110a-c**

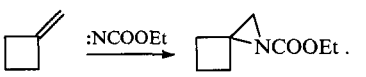
R = Me, $Pr^n$, $Pr^i$ .

The cyclopropanation of MCB with methyl diazoacetate, catalysed by $Cu(acac)_2$ in $CH_2Cl_2$, is a convenient method for preparing esters of spirohexanecarboxylic acid **111**.[254]




**111** (87%)

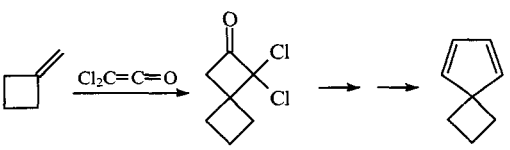
The addition of singlet ethoxycarbonylnitrene to MCB has been described.[255] This reaction gives the azaspirane **112** in a moderate yield:




**112** (45%)

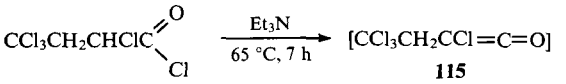
### 2. [2 + 2]-Cycloaddition

The cycloaddition to MCB of dichloroketene, generated in situ from dichloroacetyl chloride, yielded the adduct **113**.[256] This ketone has been used in the synthesis of spiro[3.4]octa-5,7-diene **114**:[257]

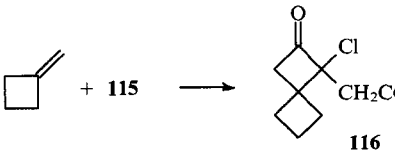



**113** (60%) **114**

The interaction of MCB with tetrachlorobutanoyl chloride in the presence of $Et_3N$ proceeds in a similar way:[258]



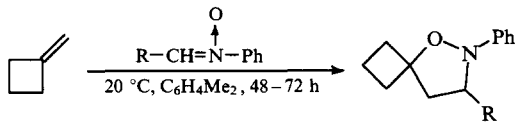

**115**




**116**

### 3. [2 + 3]-Cycloaddition

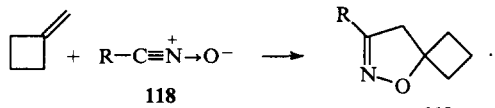
A convenient way of synthesising spirane isoxazolidines **117** incorporating a cyclobutane ring in yields of 70% or more is based on the 1,3-dipolar cycloaddition of *N*,*C*-disubstituted nitrones to MCB.[259,260]




**117**

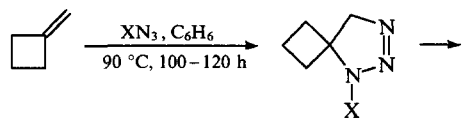
R = Ph, PhCO, PhNHCO, $XC_6H_4NHCO$ (X = Br, Me, Ac, EtO).

The cycloaddition of the *N*-oxides **118** to MCB is a convenient single-stage method for the synthesis of spiro(4,5-dihydroisoxazole-5,1-cyclobutanes) **119**:[261–263]

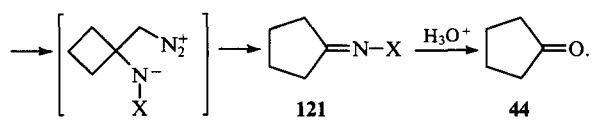



**118** **119**

*p*-Nitrobenzenesulfonyl azide reacts with MCB via a 1,3-dipolar cycloaddition mechanism to give the triazoline intermediate **120**, which undergoes rapid rearrangement with ring expansion, affording the sulfonimide **121**. The latter is hydrolysed to give cyclopentanone:[264]

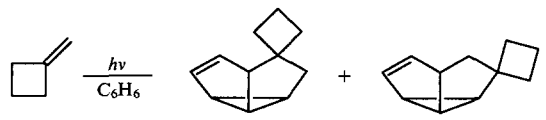



**120**




**121** **44**

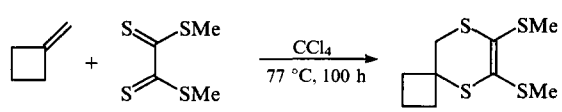
An unusual cycloaddition has been observed on irradiating MCB in benzene; equal amounts of the cyclic adducts **122** and **123** (overall yield 5%) were obtained:[265]




**122** **123**

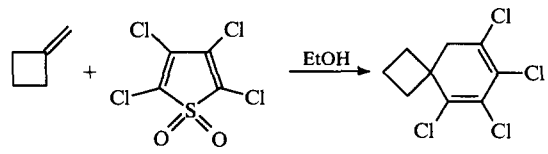
### 4. [2 + 4]-Cycloaddition

The interaction of MCB with dimethyl tetrathiooxalate occurs similarly to the Diels–Alder reaction in which MCB acts as the dienophile:[266]



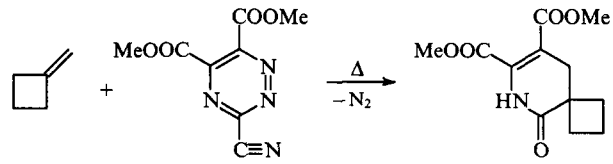

**124** (75 %)

An unusual example of the formation of the cyclic adduct **125** from MCB and tetrachlorothiophene dioxide has been described by Raasch.[267]



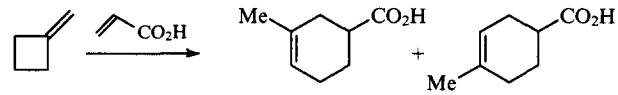

**125** (75%)

The triazine **126** reacts with MCB in a similar way (with the cleavage of the heterocyclic ring and liberation of nitrogen).[268]




**126** **127**

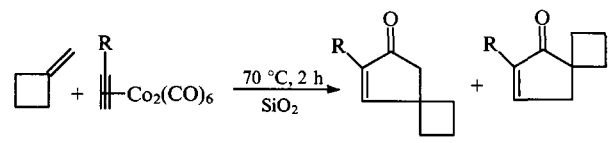
Methylenecyclobutane can enter into the Diels–Alder reaction, acting as the diene.[164]




**128** **129**

### 5. [2 + 2 + 1]-Cycloaddition

The cycloaddition to MCB of alkynes bound into a complex with cobalt carbonyl (one of the coordinated CO molecules participates in the reaction) yields a mixture of the spiroketones **130** and **131** in a ratio of 1 : 1.[269,270]




**130** **131**

47% (R = Me);
89% (R = Ph)

## VIII. Reactions with ring opening

The opening of the MCB ring has been observed in its reactions with hydroxyl or methyl radicals.[271,272]

The thermal decomposition of MCB has been studied.[273–276] The Arrhenius parameters of this process were determined in the same investigations.

The photolysis of MCB leads to equimolar amounts of ethene and allene.[277,278] Vacuum UV photolysis (Xe 147.0 nm and Kr 123.6 nm) occurs less selectively.[279,280] Among the photolysis products, $H_2$, $C_2H_2$, $C_2H_4$, allene, methylethyne, vinylethyne, and buta-1,3-diene were detected.

The rearrangements of MCB accompanied by its decomposition have been discussed in a review.[281]

## IX. Polymerisation

The possibilities of using MCB for preparing polymers and copolymers have been examined.

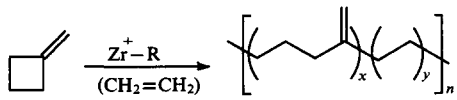
Methylenecyclobutane and some of its derivatives (3-CN, 3-COOH, 3-Me-3-COOH, 3-Ph) do not polymerise in the

presence of radical initiators,[282,283] $BF_3 \cdot Et_2O$, or BuLi, but they form copolymers with acrylonitrile, styrene, or methyl methacrylate.[282]

The polymerisation of MCB on treatment with Lewis acids ($AlCl_3$, $TiCl_4$, $SnCl_4$, or $BF_3$) results in a low-molecular-mass polymer (average molecular mass < 2000) having a regular structure with cyclobutane side groups.[284]

In the presence of Ziegler–Natta catalysts [$AlEt_3-Ti(OPr)_4$ or $AlEt_3-TiCl_4-PPh_3$], poly(methylenecyclobutane) is formed, the ozonisation of which yields a linear polyketone.[285] When other catalysts were employed, polymerisation occurred with complete or partial opening of the cyclobutane rings.[286–288]

The regioselective polymerisation of MCB and its regioselective copolymerisation with ethene occur on treatment with $[(1,2\text{-}Me_2C_5H_3)_2ZrMe]^+[MeB(C_6F_5)_3]^-$ [289,290] to yield a linear polymer or copolymer **132** with methylene side groups.




**132**

The influence of MCB on the polymerisation of isoprene in the presence of the Ziegler–Natta catalyst $Al(Bu^i)_3-TiCl_4$ has been studied by Sire et al.[291] It was found that an admixture of MCB in the monomer has no effect on the properties of the polymer, but substantially retards the polymerisation.

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