Russian Chemical Reviews **62** (4) 337–358 (1993)
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UDC 547.512

The chemistry of acetylcyclopropane

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Contents

I. Introduction	337
II. Methods of synthesis of acetylcyclopropane	337
III. Chemical properties of acetylcyclopropane	338
IV. The use of acetylcyclopropane in the synthesis of natural and practically useful compounds	352

Abstract. Data on the synthesis chemical reactions of acetylcyclopropane are presented. A systematic account is given in terms of the reactions of the functional groups of the above compound (methyl, carbonyl, and cyclopropyl). The extensive possibilities of acetylcyclopropane as a convenient five-carbon building block in organic synthesis are demonstrated. The bibliography includes 268 references.

I. Introduction

During the more than one hundred years that have elapsed since W A Perkin, Jr[1] first described the synthesis of acetylcyclopropane (ACP) and especially during the last decades, extensive structural data have accumulated on the use of this five-carbon synthon in organic synthesis. The presence of the keto-group in acetylcyclopropane in combination with a three-membered carbocycle is responsible for the specific bifunctional properties of this compound and, apart from the multiplicity of classical reactions characteristic of methyl ketones, it is possible to carry out with this compound also reactions involving the opening and retention of the cyclopropane fragment. Organic compounds of various classes have been synthesised from acetylcyclopropane. Acetylcyclopropane and its derivatives are widely used in the preparation of substances which have found applications in engineering, agriculture, and medicine.

Despite the existence of fairly extensive data on the chemical reactions of acetylcyclopropane, they have not so far been treated systematically and the present review was undertaken to fill this gap.

II. Methods of synthesis of acetylcyclopropane

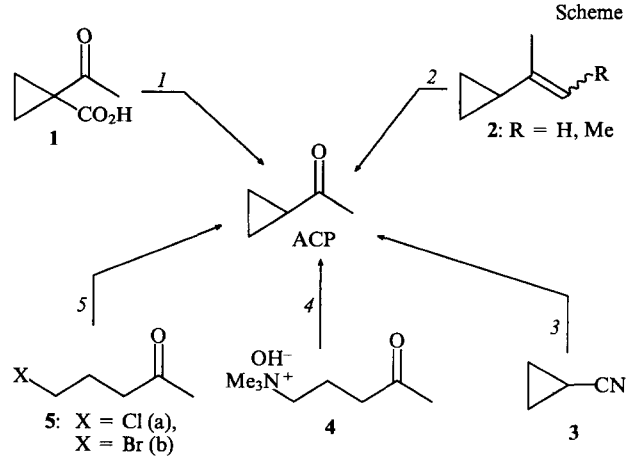
Acetylcyclopropane was first synthesised in a moderate yield in 1887 by the thermolysis of acetylcyclopropanecarboxylic acid **1** (Scheme 1).[1] At the present time, acetylcyclopropane is a commercially available product. A compilation of the methods of its synthesis known at the end of the 1950s has been published.[2]

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Received 3rd February 1993
Uspekhi Khimii **62** (4) 365–386 (1993); translated by A K Grzybowski

Apart from the thermolysis mentioned above, these include the oxidation of alkenes **2**.[3,4] Grignard synthesis from the cyano-derivatives **3**,[5] thermal decomposition of the ammonium salt **4** in the presence of KOH,[6] as well as cyclisation of γ-acetylpropyl halides **5**.[2] These and related methods are in fact most widely used.

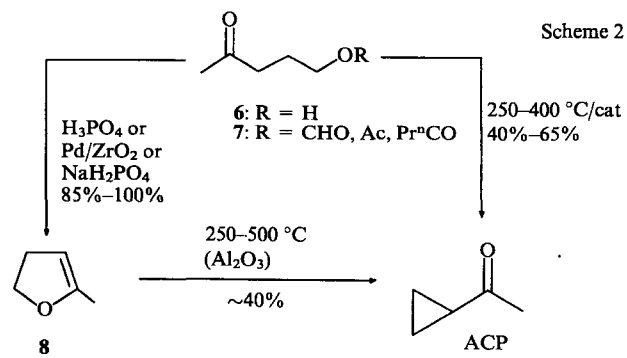
Scheme 1



(*1*) Δ(30%);
(*2*) $KMnO_4$ or O_3 (~50%);
(*3*) MeMgBr (40%);
(*4*) Δ/KOH (45%);
(*5*) EtONa or KOH (40%–95%).

The methods of synthesis of acetylcyclopropane developed during the last three decades, among which special mention should be made of the synthesis of acetylcyclopropane from acetylpropyl alcohol **6** and some of its derivatives, are summarised below (Scheme 2).[7–13]

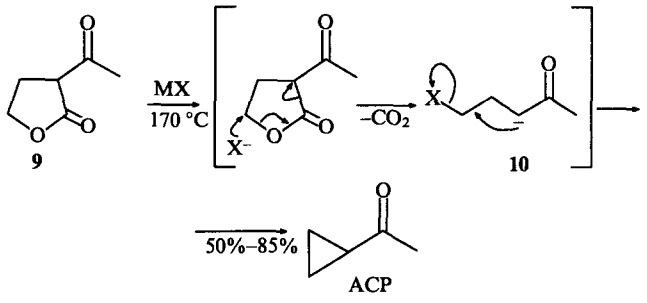
Scheme 2



The cyclodehydration of compound **6** proceeds readily and affords the dihydrofuran **8**,[7,14,15] the (thermo)catalytic isomerisation of which in a flow system leads to acetylcyclopropane.[7-11,13,16] The efficiency of this stage depends on a series of parameters (the temperatures used, contact time with the catalyst, etc.) and can reach 40% for a low overall conversion of the ketoalcohol **6**. The use of the esters **7** makes it possible to increase the yield of acetylcyclopropane to 65%.[11,12] The catalysts used in this process are zeolites[12] or metal oxides, mainly transition metal oxides.[11,12]

Acetylcyclopropane can be obtained by the thermolysis of α-acetylbutyrolactone **9** in the presence of catalytic amounts of alkali ,metal halides (Scheme 3).[17-20]

Scheme 3

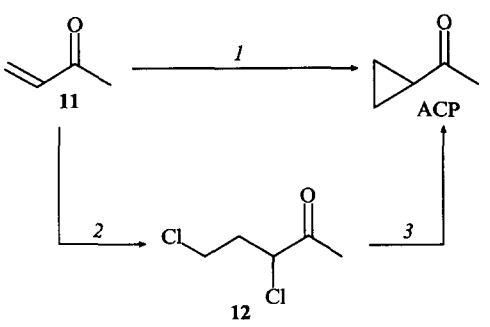


MX = NaI, NaBr, LiCl.

The reaction evidently proceeds via stages involving the opening of the five-membered ring and the generation of the carbanion **10**, which subsequently undergoes intramolecular cyclisation.[17,18] The maximum yield of acetylcyclopropane was achieved under these conditions using NaI in hexamethylphosphoramide (HMPA).[17]

One of the evident approaches to the synthesis of acetylcyclopropane involves the transformation of methyl vinyl ketone **11** (Scheme 4).

Scheme 4

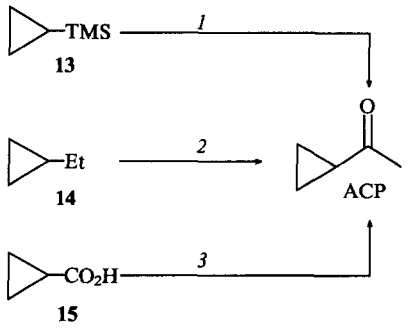


(*1*) CH_2I_2–Zn/Cu (50%), CH_2I_2–Zn/Ag (60%), CH_2Br_2–Ni(0)/Zn/NaI (> 95%);
(*2*) CH_2Cl_2/MeCN, CuCl, Bu^n_4NBr, *hν*;
(*3*) e^- (45% from **11**).

The classical version of the Simmons–Smith reaction leads in this instance to acetylcyclopropane in approximately 50% yield.[21] The use of a modified version of this method, in which the Zn/Cu couple has been replaced by the Zn/Ag couple, proved to be somewhat more effective.[21] A virtually quantitative yield of acetylcyclopropane was achieved when CH_2Br_2 and the complex Ni(0)/Zn/NaI were involved in the reaction.[22] Finally, the possibility of converting compound **11** into a cyclopropane derivative using CH_2Cl_2 as the methylenating agent has been demonstrated by the two-stage version of this process, including the cathodic dechlorination of the intermediate photoadduct **12**.[23]

A small group of methods is based on the use of cyclopropane precursors (Scheme 5). Thus the acylation, catalysed by a Lewis acid, of the cyclopropylsilane **13**, which was obtained in its turn by the Simmons–Smith conversion of trimethylvinylsilane into a cyclopropane derivative, leads smoothly to acetylcyclopropane virtually without the competing reaction involving the opening of the three-membered ring.[24] The oxidation of ethylcyclopropane **14** by ozone in the presence of SiO_2 is also characterised by a satisfactory yield of acetylcyclopropane.[25] The single-stage conversion of the acid **15** into acetylcyclopropane on treatment with LiMe,[26] in principle related to the conversion into acetylcyclopropane of the nitrile **3** of the above acid on treatment with MeMgBr, is almost just as effective.

Scheme 5



(*1*) AcCl/$AlCl_3$–CH_2Cl_2 (60%);
(*2*) O_3/SiO_2 (~60%);
(*3*) MeLi (~65%).

It follows from the data presented that, among the various methods of synthesis of acetylcyclopropane available at present, the procedures based on γ-acetylpropyl chloride **5a** and the corresponding alcohol **6** are the most attractive and technologically most sophisticated.

III. Chemical properties of acetylcyclopropane

Numerous reactions of acetylcyclopropane, occurring both with participation of its carbonyl or methyl group and with the opening of the three-membered carbocycle, have now been described. This will be the subject of the further consideration of the literature data available at present, which do not so far contain information about the direct introduction of functional groups into the cyclopropane fragment of this molecule.

1. Reactions involving the carbonyl group

Reactions of this type constitute the commonest series of reactions of acetylcyclopropane. They are similar to the known reactions of aliphatic ketones.

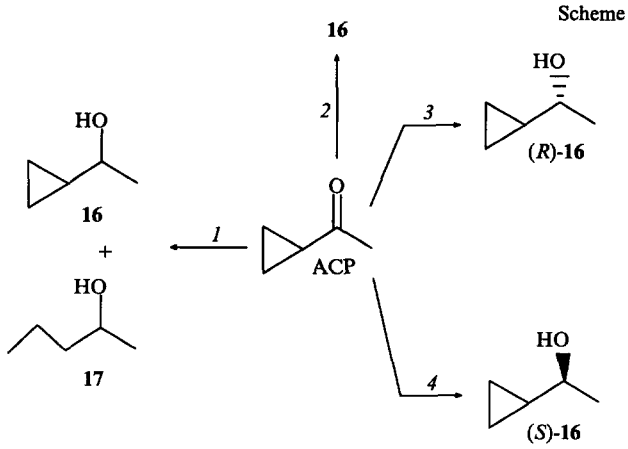
a. Reduction

Acetylcyclopropane is an extremely popular substrate for the study of the properties of new reductants. In particular, it has become one of the first objects to which the Bouveault–Blanc reaction has been applied.[27] The reduction of acetylcyclopropane by the Bouveault–Blanc method leads to a mixture of secondary alcohols with cyclic (compound **16**) and linear (compound **17**) structures (Scheme 6).[27,29] Hydrogenation of acetylcyclopropane over a nickel catalyst is also accompanied to a significant extent by the opening of the three-membered ring,[28] which can be appreciably suppressed by using platinum[30] and can be almost entirely excluded in the presence of a chromium-containing catalyst.[28] The complete retention of the cyclopropane ring is attained when a zinc-based catalyst is employed,[31,32] although the degree of conversion of acetylcyclopropane is then fairly low.

Acetylcyclopropane is reduced chemoselectively by Bu^n_3SnH under mild conditions but with a moderate yield.[33] The Meerwein–Pondorf reduction of acetylcyclopropane makes it possible to obtain the alcohol **16** in ~90% yield[29] under

conditions involving the rapid decomposition of the intermediate organoaluminium complexes, inducing the formation of high-molecular-mass side products.[34] The same complications may arise in the treatment of the reaction mixtures formed as a result of the hydride reduction of the acetylcyclopropane with the aid of lithium tetrahydroaluminate ($LiAlH_4$)[28,31,35-39] or KBH_4.[40]

Scheme 6



(*1*) Na/EtOH (~50%), H_2/Ni-Ra (~70%, **16**:**17** ≃1:1), H_2/Pt (~50%), H_2/Cr_2O_3, 100°C (90%);
(*2*) H_2/Zn, 160°C (45%), H_2/Zn–Cu, 125°C (65%), Bu^n_3SnH/Bu^n_4NCl (~25%), Bu^n_3SnH/Bu^n_4NF (~45%), $(Pr^iO)_3Al/Pr^iOH$ (~90%), $LiAlH_4/Et_2O$ (~75%), KBH_4/MeOH (~75%);
(*3*) enzymes from the fungus *Pseudomonas* (> 60%);
(*4*) (*R*)-β-isopinocamphenyl-9-borabicyclo[3.3.1]nonane.

Data on the enantioselective reduction of acetylcyclopropane have been published recently. Thus the chemoenzymic method, using the enzyme system from fungi of the genus *Pseudomonas*, makes it possible to obtain the optically pure (> 98%) isomer (*R*)-**16** in a satisfactory yield.[41-43] Its enantiomer (*S*)-**16** has been synthesised with an optical purity of 69% with the aid of the bulk-phase chiral tetrahydroborate reagent.[44]

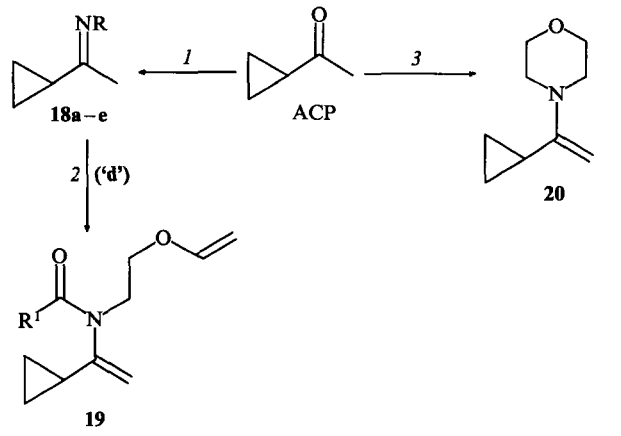
b. Synthesis of nitrogen-containing derivatives

The interaction of acetylcyclopropane with various nitrogen-containing bases afforded a large number of its different derivatives involving the carbonyl group—from the simple oxime[45,46] and hydrazones[47-54] to structurally more complex systems, some of which serve as the starting materials in the synthesis of medicinal preparations and herbicides.[46,49,55-58]

The interaction of acetylcyclopropane with primary amines leads smoothly to the Schiff bases **18a–e** (Scheme 7),[58-63] which have recently found synthetic applications on an increasingly wide scale. In particular, the acylation of the imine **18d** leads to the smooth formation of the vinylamides **19**, which are of interest as monomers; in this reaction, only the nitrogen atom is subjected to electrophilic attack in the initial molecule.[61-63] The direct conversion of acetylcyclopropane into the enamine **20** has been achieved, admittedly only in a low yield, by the Lewis-base catalysed reaction of acetylcyclopropane with morpholine.[64,65]

The primary amine **21** was obtained by the reductive amination of acetylcyclopropane[66,67] (Scheme 8).† In contrast to the hydrogenation over Raney nickel, in this case the reaction is not accompanied by the opening of the cyclopropane ring, which can be explained by the partial deactivation of the catalyst in the presence of NH_3.[66] Nucleophilic substitution of the hydroxy-group by the amino-group in the intermediate cyanohydrins, arising in the interaction of acetylcyclopropane with HCN, leads to the aminonitriles **22a**[55,56,68] and **22b**.[69]

Scheme 7



18: R = Bu^n(**a**), cyclo-C_6H_{11}(**b**), CH_2CH_2OEt (**c**), $CH_2CH_2OCH=CH_2$ (**d**), $CH_2CH_2CO_2TMS$ (**e**),
19: R^1 = Me, Et, Pr^n, Bu^n, Ph

(*1*) RNH_2/H^+, boiling PhH (50% – 90%);
(*2*) R^1COCl/NEt_3, PhH (70% – 80%);
(*3*) morpholine/$TiCl_4$, pentane (> 30%).

The reaction of acetylcyclopropane with *o*-phenylenediamine affords the aminal **23**.[70] Another representative of substances of this class is the amidonitrile **24**, which exhibits mutagenic properties. It was synthesised by the condensation of 2-cyano-aziridine with acetylcyclopropane and subsequent hydrolysis of one of the two nitrile groups in the molecule of the intermediate adduct.[57]

Individual α-cyclopropyl-containing secondary amines have been obtained from the Schiff bases **18a–d**. Thus the aminoester **25** has been synthesised in an almost quantitative yield by the hydride reduction of the imine **18d**.[61] The alkoxide-catalysed addition of dialkyl phosphites to the azomethine bond in the imines **18a–d** involves the Arbuzov rearrangement, affording high yields of the aminoalkylphosphonates **26a–d**, among which compounds with insecticidal properties were found.[58]

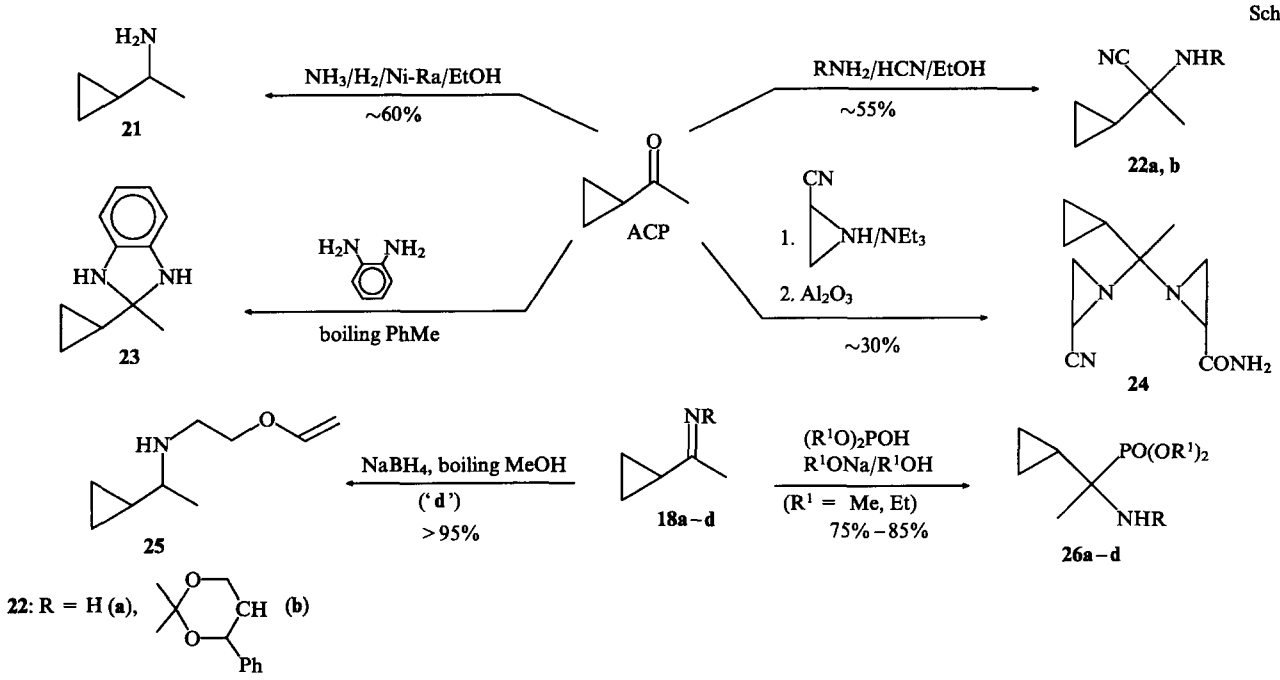
c. Enolic derivatives of acetylcyclopropane

On treatment with strong bases of the type of lithium tetramethylpiperidide (LTMP),[71] lithium diisopropylamide (LDA),[72] $NaNH_2$,[73] KH,[74] LiH,[75] and even NEt_3,[20,76-79] acetylcyclopropane is deprotonated under mild conditions, which leads to a simple and regioselective synthesis of its enolic derivatives (Scheme 9). Thus treatment of lithium acetylcyclopropane enolate with isobutyl chlorocarbonate leads to the smooth formation of the enol carbonate **27**.[71] The TMS-ester‡ **28**, which has found extensive synthetic applications, is obtained similarly to the interaction of Me_3SiCl with the acetylcyclopropane enolate generated *in situ* by various methods,[20,72-74,76-79] for example by treatment with NEt_3 in dimethyl formamide (DMF).[76-79] The yield of compound **28** is in this case ~65%, diminishing somewhat when catalytic amounts of $ZnCl_2$ are used,[20] although overall this version of the silylation reaction is comparatively more convenient, because it simplifies the isolation of the ether. The deprotonation of acetylcyclopropane with the aid of LDA, $NaNH_2$, or KH promotes an increase in the yield of compound **28**. The LiH obtained *in situ* by the hydrogenation of the complex Bu^nLi-TMEDA (TMEDA = tetramethylethylenediamine) partly reduces acetylcyclopropane, affording, after treating the reaction

† The absence from the schemes of information about the yield and/or the proportions of the products (for example, in ACI[e] → **23**) always implies the absence of such data from the original sources.

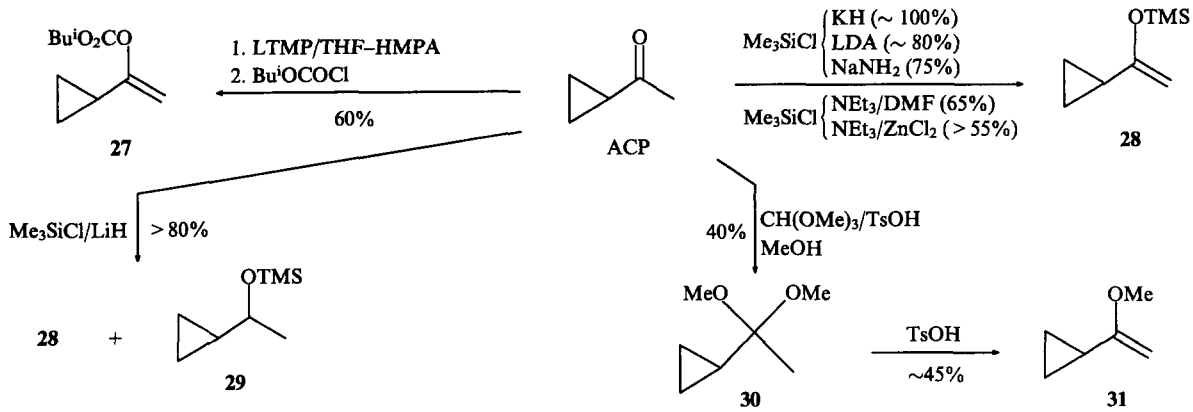
‡ TMS = trimethylsilyl (translator).

Scheme 8



26: R = Bu^n (a), cyclo-C_6H_{11} (b), CH_2CH_2OEt (c), $CH_2CH_2OCH=CH_2$ (d).

Scheme 9



mass with Me_3SiCl, a mixture of the ethers **28** and **29** in proportions of ~2:3.[75]

The methyl ether **31** was synthesised in a moderate yield by eliminating the elements of MeOH from the dimethyl ketal **30** obtained by a standard method.[80]

d. Conversion into olefins and related reactions of acetylcyclopropane

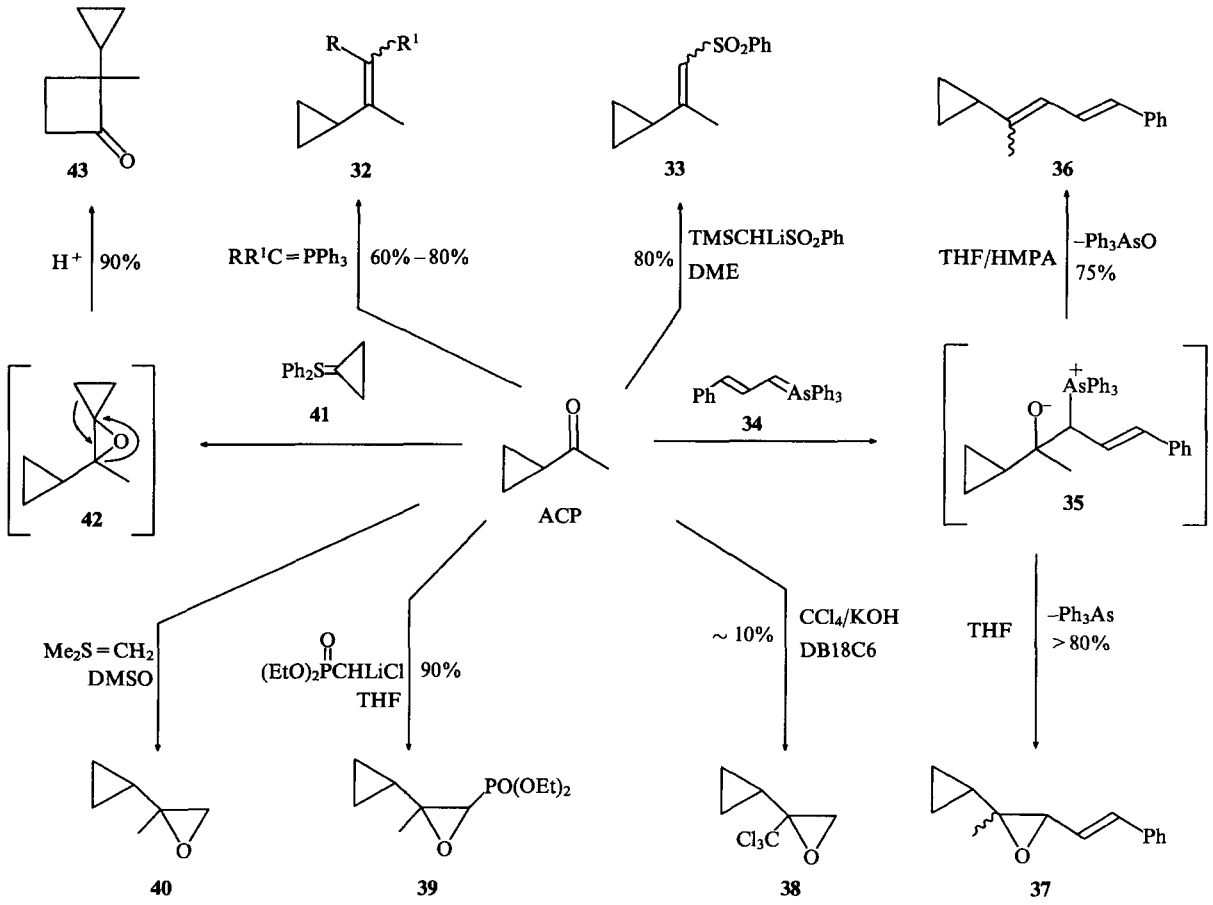
Reactions of acetylcyclopropane with phosphorus, arsenic, and sulfur ylides, leading to the corresponding olefins and epoxides, are widely represented in the literature. For example, the Wittig conversion of acetylcyclopropane into olefins proceeds without complications, affording vinylcyclopropanes **32** in preparative yields and with the expected ratio of the stereoisomers[81–87] (Scheme 10). The Peterson reaction of acetylcyclopropane with the lithio-derivative of trimethylsilylbenzenesulfonylmethane leads similarly to the smooth formation of a mixture of the vinyl sulfones **33** ($Z:E \simeq 3:1$).[88]

The arsorane **34** interacts with acetylcyclopropane via one of two possible pathways depending on the reaction conditions. Thus, when a 1:1 THF–HMPA (HMPA = hexamethylphosphoramide) mixture was used as the solvent, the product **36** of the olefin formation reaction was obtained exclusively ($E:Z \simeq 1:1$),[89,90] whereas in tetrahydrofuran (THF) only the epoxide **37** is formed.[89] The authors correctly explain this effect by the ability of HMPA to stabilise the positive charge in the betaine intermediate **35**, which should diminish the polarity of the C–As bond and thereby promote the generation of the alkene.[89]

The substituted oxiran **38** has been synthesised by the reaction of acetylcyclopropane with CCl_4 in the presence of alkali and the crown-ether, although the yield was low.[91] The mechanism of this reaction has not been explained.

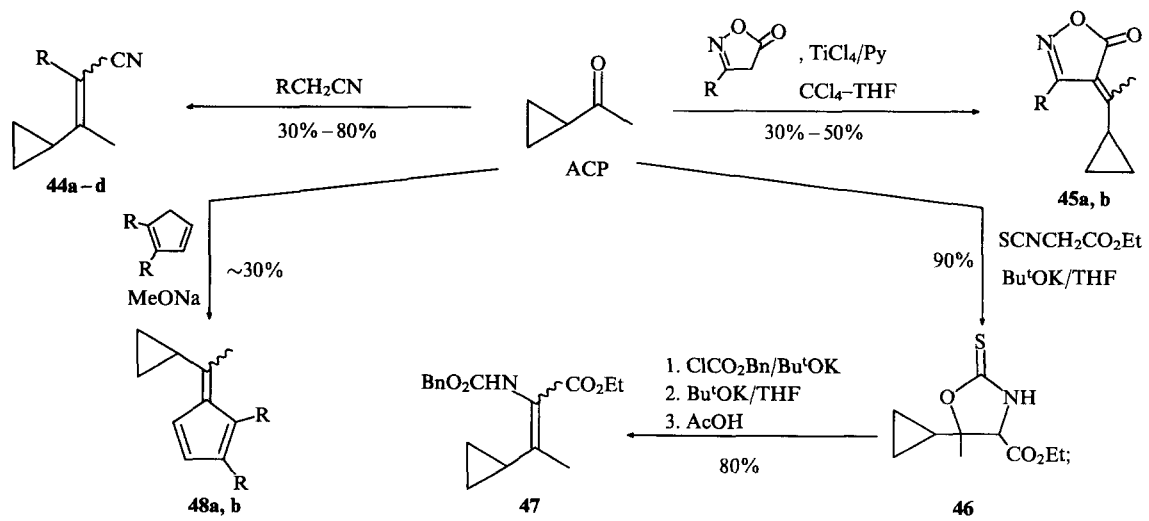
The epoxide **39** has been obtained almost quantitatively by condensing acetylcyclopropane with the lithio-derivative of diethyl chloromethylphosphonate, evidently via an intermediate chlorohydrin stage.[92] This reaction is in principle related to the Corey–Chaykovsky reaction with the sole difference that the leaving group is in this instance the chlorine atom and not the sulfonium group. The involvement in this reaction of acetylcyclopropane and dimethylsulfonium methylide leads to the epoxide **40**.[93] The analogous interaction with the ylide **41** affords a high yield of the cyclobutanone **43**, which evidently arises as a result of the ready rearrangement of the intermediate spiroepoxide **42**.[94,95]

Scheme 10



32: R = H, R^1 = Me, OMe; R = R^1 = Me; RR^1 = $(CH_2)_2$, $(CH_2)_3$;
DB18C6 = dibenzo-18-crown-6.

Scheme 11



44: R = CN (**a**), Bz (**b**), CO_2Et (**c**), $CONH_2$ (**d**);
45: R = Me (**a**), Ph (**b**);
48: R = H (**a**), RR = $(CH=CH)_2$ (**b**);
Bn = benzyl, Bz = benzoyl.

The Knoevenagel reaction with participation of acetylcyclopropane has been used to obtain the unsaturated nitriles **44a–d**[96,97] (Scheme 11), which have served, in their turn, as key intermediates in the synthesis of 2-aminothiophenes and some of their derivatives with antitumour activity. It is noteworthy that the effectiveness of the condensation depends on the nature of both the initial malononitrile and the chosen catalyst. For example, on catalysis with an ion-exchange resin[97] or an AcOH/$AcONH_4$ mixture,[98] the yield of the dinitrile **44a** (or the ester **44c**) is 50%, falling to 30% in the case of the amide **44d**.[97] The use of the AcOH–β-alanine system as the catalyst makes it possible to obtain the nitriles **44a**[99] and **44b**[96] in 81% and 58% yields respectively. The stereochemistry of the olefins **44b–d** remains unelucidated.

The Lewis acid-catalysed condensation of acetylcyclopropane with 3-methylisoxazolone leads stereoselectively to the adduct **45a**, which is a mixture of isomers ($E:Z$ = 85:15).[100] In the case of the 3-phenyl derivative, both stereoisomers of compound **45b** are formed in approximately equal amounts.[100]

The reaction of ethyl isothiocyanatoacetate with acetylcyclopropane in the presence of *tert*-BuOK affords the oxazolidinethione **46** as a result of the intermolecular cyclisation of the intermediate tertiary alcohol.[101,102] The product of the acylation of compound **46** isomerises under the influence of the excess of *tert*-BuOK, which is accompanied by the elimination of COS. This leads ultimately to the vinylcyclopropanes **47** in an overall yield >70%.[102] Finally, condensation of acetylcyclopropane with CH acids, catalysed by a strong base, led to the formation of the corresponding fulvenes **48a**[103] and **48b**[104] in moderate yields.

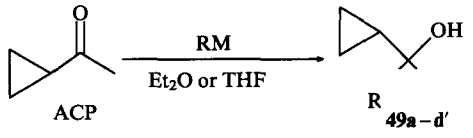
Thus conversion into olefins and nucleophilic reactions of acetylcyclopropane of a similar nature provide an easy access to functionalised vinylcyclopropanes and related epoxides, which have a high synthetic potential.

e. Reactions of acetylcyclopropane with organometallic compounds

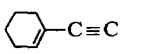
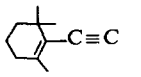
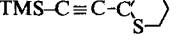
The data described above cover only a small number of examples of the use of acetylcyclopropane as a convenient and readily available compound for the study of the properties of various nucleophiles, leading at the same time to products with a wide variety of synthetic applications. The main bulk of the data published until recently refer to the synthesis and subsequent chemical reactions of cyclopropyl alcohols **49** formed in the reactions of acetylcyclopropane with various organometallic compounds—primarily with Grignard reagents (Scheme 12).

It is seen from the data presented that the Grignard reaction involving acetylcyclopropane proceeds as a whole with fairly high yields, which decrease, as was to be expected, when sterically bulky allyl halides are used. In the case of MeMgI, a significant amount (~15%) of 1-iodo-4-methylpent-3-ene—the acyclic product of the cyclopropylcarbinyl rearrangement (CPCR)—is

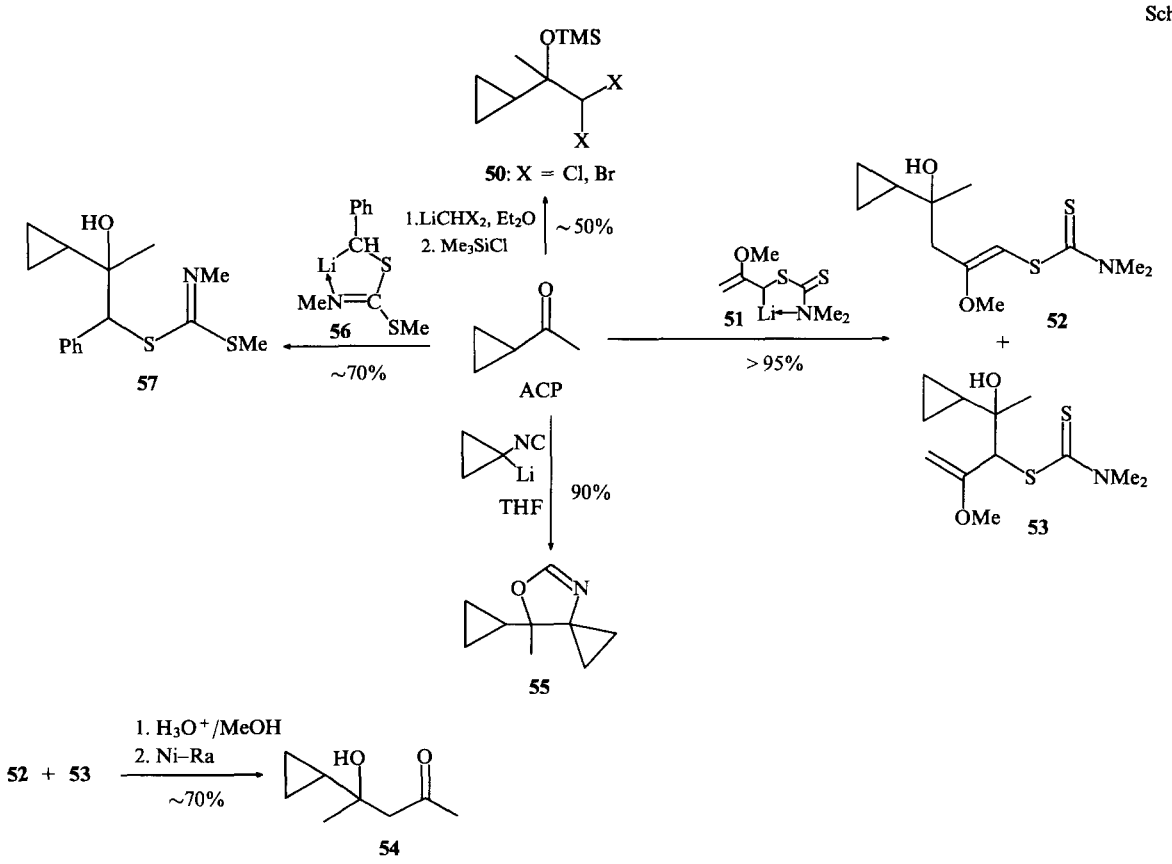
Scheme 12



M = Li, Na, K, MgCl, MgBr, MgI

No.	R	M	Yield of **49** (%)	Ref.
a	Me	Li	61	105
		MgX (X = Cl, Br, I)	55–90	34, 106–115
b	Et	MgBr	54–81	107, 109, 112, 113, 116–119
c	Pr^n	MgX (X = Cl, Br)	51–57	107, 120–122
d	Pr^i	MgBr	27–51	123
e	Bu^n	MgBr	52–84	107, 124, 125
f	Bu^t	MgCl	19	126
g	$HO(CH_2)_4$	MgCl	81	127
h	$CH_2=CH$	MgX (X = Cl, Br)	50–83	128–130
i	(*Z*)-MeCH=CH	MgBr	82	131
k	$CH_2=CHCH_2$	MgBr	48–96	131–134
l	(*E*)-$MeCH=CH(CH_2)_2$	MgBr	>70	135, 136
m	$EtMeC=CH(CH_2)_2$	MgBr	72	136
n	$CH_2=CHCMe=CH(CH_2)_2$	MgBr	94	129
o	$Pent^iMeC=CH(CH_2)_2$	MgBr	57	136
p	$H(CH_2CMe=CHCH_2)_nCH_2$			
	$n=1$	MgBr	70–91	110, 111, 136, 137
	$n=2$	MgBr	46–69	110, 111, 132, 136
	$n=3$	MgBr	57	111
r	Ph	Li	>91	138
		MgBr	57–65	139, 140
s	Bn	MgX (X = Cl, Br)	57–85	141, 142
t	*o*-$CNC_6H_4CH_2$	Li	~100	143
u	$HC\equiv C$	Na	77–88	129, 144, 145
		K	50–90	146–148
v	$MeC\equiv C$	MgBr	90	131
w	cyclo-$PrC\equiv C$	Li	82	149
		MgBr	73	149
x		MgBr	80	150
y		MgBr	80	150
z	$PhC\equiv C$	K	84	151
		MgBr	95	151
a'	$HOCH_2C\equiv C$	K	70	132
b'	$HC\equiv C-CH_2$	MgBr	88	131
c'	$C(SMe)_3$	Li	83	152, 153
d'		Li	78	154

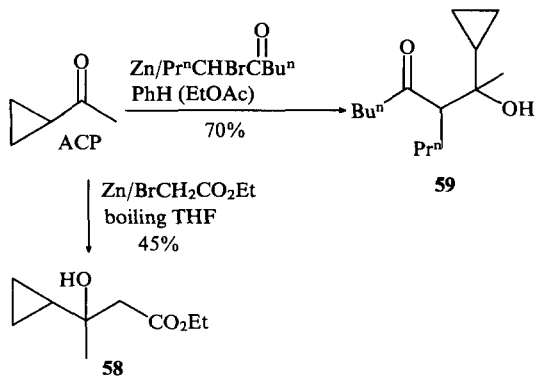
Scheme 13



formed together with the corresponding cyclopropyldimethylcarbinol **49a**.[112,114] Sodium[129,144,145] and potassium acetylides[132,146–148,151] interact with acetylcyclopropane without complications, affording the corresponding ethynylmethylcarbinols. Substituted acetylides have been used successfully under these conditions as Iotsich reagents or as alkali metal derivatives.

Examples of the interaction of certain functionalised organolithium reagents are presented in Scheme 13. Thus silylation of the products of the condensation of dihalomethyllithium with acetylcyclopropane leads to the trimethylsilyl ether **50**, which can readily undergo β-elimination on treatment with bases to form *gem*-dihaloalkenes.[155] The introduction of the acetonyl fragment into the acetylcyclopropane molecule has been achieved with the aid of the lithio-derivative of the dithiocarbamate **51**, which interacts with acetylcyclopropane, affording a mixture of the regioisomers **52** and **53** in proportions of 4 : 1.[156] Their hydrolysis and subsequent reductive desulfurisation of the intermediate dithio-carbamates led to the formation of the β-hydroxyketone **54** in a high overall yield.

Scheme 14

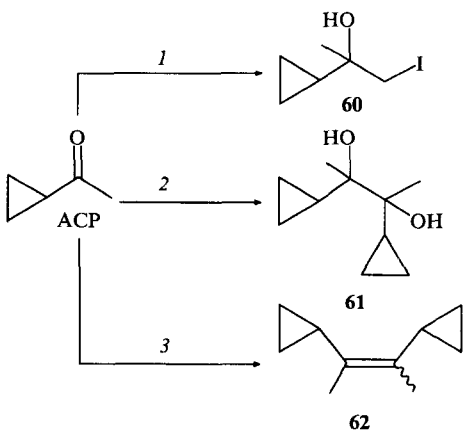


The reaction of the lithio-derivative of isocyanocyclopropane with acetylcyclopropane leads to an intermediate isocyano-derivative, which undergoes spontaneous intramolecular cyclisation to the oxazoline **55**.[157] Yet another example of the use of acetylcyclopropane for the synthesis of various heterocycles is provided by its reaction with the metallated dithioimide **56**, which leads to the carbinol **57** — a precursor of oxathiolans.[158]

Another interesting but hitherto inadequately developed approach to the synthesis of functionalised cyclopropylmethylcarbinols involves the use of organozinc reagents. For example, the synthesis of the tertiary alcohols **58**[159] and **59**[160] from acetylcyclopropane by the Reformatskii reaction has been described (Scheme 14).

The radical–ion reactions with participation of acetylcyclopropane have also been investigated extremely inadequately.

Scheme 15



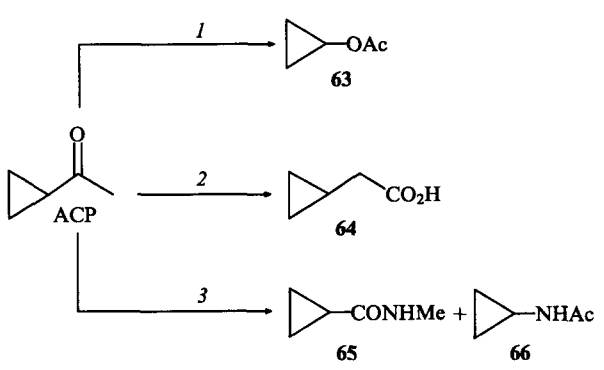
(*1*) CH_2I_2/Sm(0)–THF (60%);
(*2*) Al/Hg (30%), $TiCl_4$/Mg–Bu^{t}OH (60%);
(*3*) $TiCl_3$/$LiAlH_4$–THF (30%).

Reactions of this kind include, for example, the Sm(0)-initiated iodomethylation of acetylcyclopropane with CH_2I_2, which leads effectively to the iodohydrin **60** related to the carbinols **49**[161] (Scheme 15). The conversion of acetylcyclopropane into the vicinal glycol **61**, which takes place smoothly under the influence of aluminium amalgam, also belongs to this class.[162] The yield of compound **61** increases by a factor of 2 when low-valence titanium ions, suppressing the opening of the three-membered ring, are used.[163] When the McMurry reagent[164] is employed, the final products are tetra-substituted olefins **62**, which evidently arise via the pinacol **61** stage.[165]

f. Other reactions of acetylcyclopropane involving the carbonyl group

In conclusion of this Section, we shall consider the individual reactions of acetylcyclopropane in which this compound was used simply as a standard carbonyl substrate, the products of the reaction of which have not so far found a fitting synthetic application. Thus the Baeyer–Villiger oxidation of acetylcyclopropane with the aid of CF_3CO_3H affords smoothly the acetate **63** (Scheme 16).[166] On the other hand, acetylcyclopropane is resistant to the action of weaker peracids of the type of perbenzoic acid.[167] The conversion of acetylcyclopropane into cyclopropyl acetic acid **64** by the Willgerodt–Kindler reaction takes place only with an insignificant yield.[168] Under the conditions of the Schmidt reaction, acetylcyclopropane affords a mixture of both expected regioisomeric amides **65** and **66**,[169–171] the ratio of which in a strongly acid medium depends on the pH of the reaction mixture and can be logically explained by the different rates, under such conditions, of the competing migration to the nitrogen atom of the methyl and cyclopropyl residues in the key intermediate.[170,171]

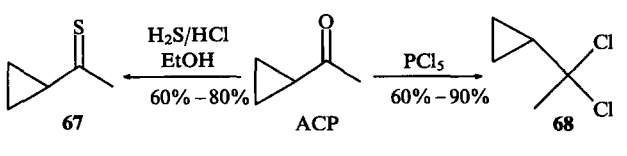
Scheme 16



(*1*) CF_3CO_3H/Na_2HPO_4 (~55%);
(*2*) S/Pi/Δ (~10%) (Pi = piperidine);
(*3*) NH_3 (90%).

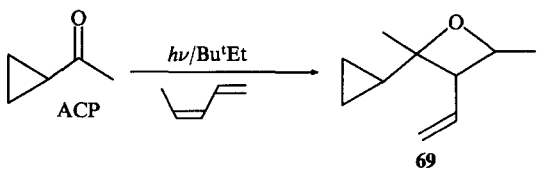
The thione **67** and the *gem*-dichloro-derivative **68**, obtained in high yields by treating acetylcyclopropane with H_2S in an alcoholic solution of HCl[172,173] and with PCl_5 in chlorinated solvents[73,174–176] respectively (Scheme 17), may be of definite synthetic interest. The yield of the dichloro-derivative **68** increases appreciably when the reaction is carried out in the presence of a base (pyridine,[177,178] Na_2CO_3[179]), although partial dehydrochlorination of the product is then observed.

Scheme 17



The photochemical [2 + 2]cycloaddition with participation of the central C=C bond of (*Z*)-piperylene and the carbonyl group of acetylcyclopropane leads regiospecifically to the oxetan **69**, the geometry of which has not been established;[180] the reaction is complicated by the formation of significant amounts of the photodimer of (*Z*)-piperylene (Scheme 18). Other examples of the involvement of acetylcyclopropane in photochemical reactions with retention of the three-membered ring are lacking in the literature.

Scheme 18



Thus the reactions with participation of the carbonyl group of acetylcyclopropane considered above illustrate the extensive possibilities of the use of this ketone for the introduction of the ethylcyclopropane carbon skeleton into various organic compounds, making available thereby a large number of oxygen- and nitrogen-containing derivatives of acetylcyclopropane — important intermediates in organic synthesis.

2. Reactions with participation of the methyl group of acetylcyclopropane

Numerous reactions based on the use of acetylcyclopropane as a typical CH acid, reacting, in contrast to other aliphatic cyclic methyl ketones, with participation of only the methyl group, have been described nowadays. Such unique regiospecificity is the main reason why ways of using acetylcyclopropane as an effective C_5 building block in the synthesis of certain biologically active substances are being sought. The activation of the carbonyl functional group of acetylcyclopropane by its conversion into the imino- or enol form proves to be superfluous in many instances, although it does promote an increase in the yield of the target product and sometimes an enhancement of the chemoselectivity of reactions with certain electrophiles.

a. Synthesis of α-functionalised derivatives of acetylcyclopropane

Treatment of acetylcyclopropane with Br_2 in methanol affords smoothly and selectively the monobromo-derivative **70**[181–185] (Scheme 19). The reaction of acetylcyclopropane with 2,4-dinitrobenzenesulfenyl chloride, leading to a virtually quantitative yield of the ketosulfide **71**, is just as selective.[186] The methanesulfonate **72a**,[187] the toluene-*p*-sulfonate **72b**,[188] and the phosphate **72c**[189] have been obtained by the reaction of acetylcyclopropane with the corresponding derivatives of trivalent iodine. In all the cases indicated, the process evidently includes a stage in which the enolic form of acetylcyclopropane is generated.[187,188]

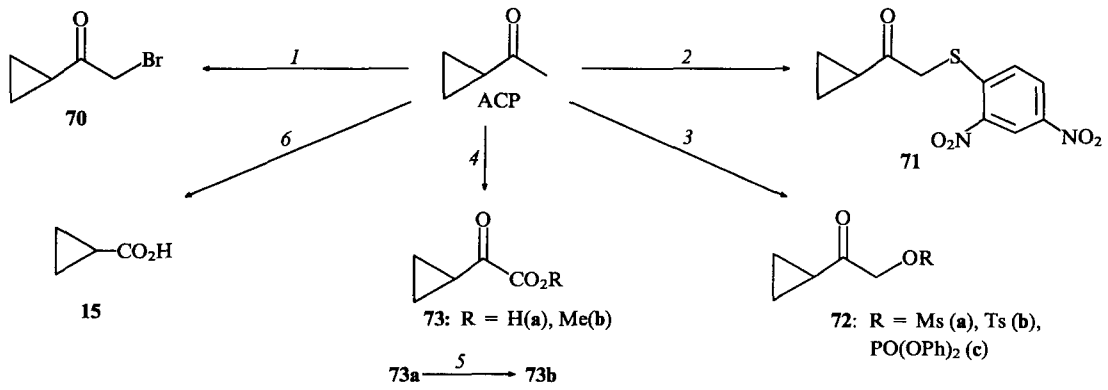
The oxidation of acetylcyclopropane with $KMnO_4$ leads to cyclopropylglyoxalic acid **73a**, which is characterised as the keto-ester **73b**.[190,191] The use of NaOBr as the oxidant opens an effective pathway to cyclopropanecarboxylic acid **15**.[70]

b. Reactions leading to the formation of a new carbon–carbon bond

The Neff methylation of acetylcyclopropane by treatment with $NaNH_2$ (Scheme 20) is characterised by low selectivity. A mixture of all three possible products **74–76** is then formed with the dimethyl derivative **74** predominating.[125]

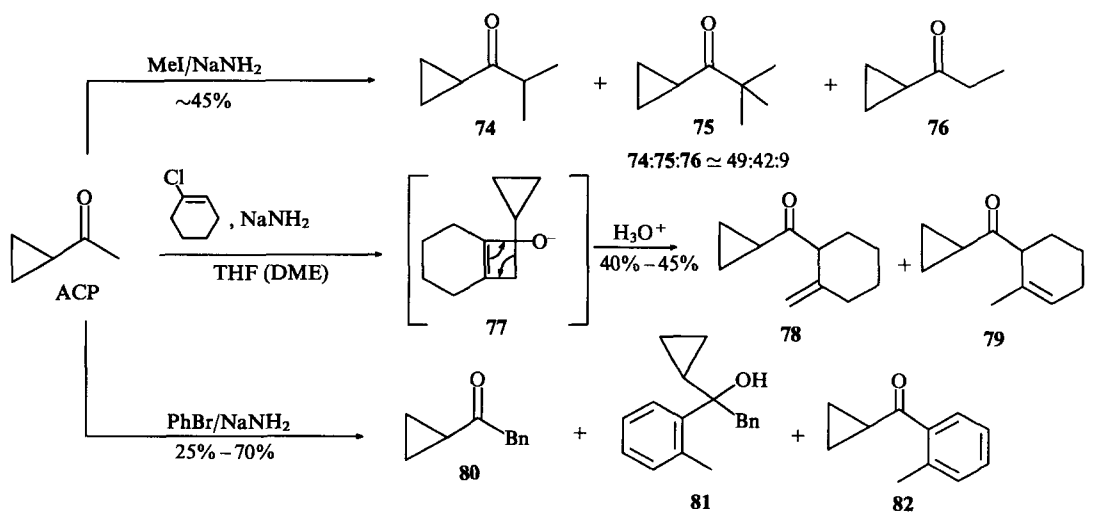
The condensation of acetylcyclopropane with 1-chlorocyclohexene in an aprotic medium, catalysed by a strong base, leads to the unsaturated ketones **78** and **79** in proportions of ~4 : 1.[192] Cyclohexyne is apparently formed initially and then interacts with the acetylcyclopropane enolate anion, affording the product **77**.

Scheme 19



(*1*) Br_2/MeOH (75%–90%);
(*2*) 2,4-$(NO_2)_2C_6H_3SCl$, boiling CCl_4 (~95%);
(*3*) PhI(OH)OR, boiling MeCN (60%–90%);
(*4*) $KMnO_4/Na_2CO_3$, H_2O–MeOH;
(*5*) CH_2N_2/Et_2O (> 60% from ACP), $Me_2SO_4/BnMe_3N^+Br^-$, H_2O–CH_2Cl_2 (> 65% from ACP);
(*6*) NaOBr, H_2O (~80%).

Scheme 20

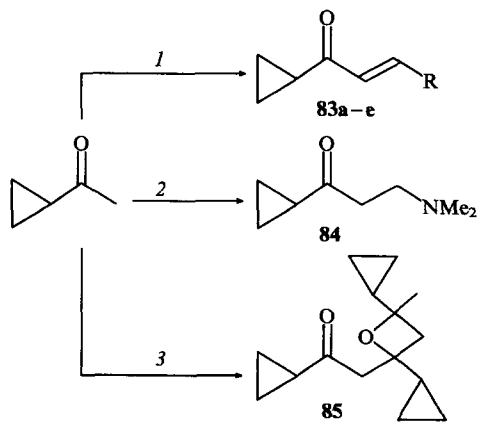


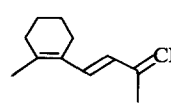
Isomerisation of the cyclobutene fragment in the adduct **77** leads to the main product **78**. Its allyl isomer **79** is probably obtained as a result of the shift of the exocyclic C = C bond on treatment with the base. The reaction of acetylcyclopropane with the dehydrobenzene generated from bromobenzene proceeds similarly, affording the product of phenylation at the methyl group **80**, the alcohol **81** and the ketone **82**, related to cyclohexene, the ratio of the latter depending on the reaction conditions.[193]

The condensation of acetylcyclopropane with trioxane in the presence of an equimolar amount of the salt CF_3CO_2H.PhNHMe affords a high yield of cyclopropyl vinyl ketone **83a**, which is evidently formed from the intermediate thermally unstable Mannich base[194] (Scheme 21). When this reaction is carried out in the classical version, the β-dimethylaminoketone **84** is formed smoothly. Its thermal decomposition led to the isolation of only the polymerisation product of the expected vinyl ketone **83a** instead of the vinyl ketone itself.[195]

Fairly numerous examples of the involvement of acetylcyclopropane in the base-catalysed condensation of the aldol-crotonic type with aliphatic[126,195–197] and aromatic[182,198–206] aldehydes have been described. The reaction undoubtedly proceeds via the corresponding aldol, which has been detected, for example, for isobutyraldehyde;[195,196] further dehydration leads to the formation of the thermodynamically preferred (*E*)-isomers **83b–e**, the yield of which depends on the nature of the aldehyde.

Scheme 21



83: R = H (**a**), Pr^i (**b**), cyclo-C_6H_{11} (**c**),  CH (**d**), Ar (**e**)

(*1*) $(CH_2O)_3/CF_3CO_2H$·PhNHMe (~75%) (for **83a**), RCHO/NaOH or Bu^{t}OK (30%–%90%) (for **83b–e**);
(*2*) CH_2O/Pr^{i}OH, Me_2NH·HCl (60%);
(*3*) KOH/Δ (25%).

The main cause of the decrease in the effectiveness of the reaction in the case of aliphatic aldehydes is their competitive reactions (self-condensation, polycondensation, and others).[195,196] The cyclopropyl tetraenyl ketone **83d**, prepared by this method (yield ~90%), was used in the synthesis of a retinal analogue.[197]

Direct condensation of the aldol–crotonic type of ketones with acetylcyclopropane is an uncharacteristic reaction in view of the tendency of the latter to form condensation products. In particular, when acetylcyclopropane was boiled (refluxed?) in the presence of powdered KOH, a compound was isolated, to which the structure of the oxetan trimer **85** with an unknown configuration was attributed.[126]

The involvement of acetylcyclopropane in a Claisen type reaction makes it possible to obtain a large series of β-dicarbonyl compounds **86** (Scheme 22). It may be catalysed by Lewis acids, for example BF_3,[207] although bases are used more often and more effectively ($NaNH_2$,[207] MeONa, EtONa,[208,209] NaH[210,211]). The result of the reaction, leading to the β-dicarbonyl derivatives **86a–g** depends significantly on the nature of the substrate. Thus condensation of acetylcyclopropane with acid anhydrides is as a rule less effective than the condensation with esters. For example, in the $NaNH_2$-initiated interaction of acetylcyclopropane with ethyl acetate, the yield of acetoacetylcyclopropane **86a** is 75%. The replacement of AcOEt by Ac_2O lowers the yield of compound **86a** almost by 20%.[207] The condensation of acetylcyclopropane with $(EtCO)_2O$, leading to the diketone **86b**, is characterised by an even lower yield (< 20%).[207]

The reaction of acetylcyclopropane with carbonates is in many respects determined by the choice of the catalyst. The best result is achieved usually when NaH is employed. Thus the replacement of $NaNH_2$ by NaH makes it possible to raise the yield of the β-ketoester **86e** from 55% to 85%.[211] Similarly diethyl oxalate reacts smoothly with acetylcyclopropane in the presence of only EtONa with formation of the highly reactive diketoester **86g**.[207] The ketoamide **87**, related to compound **86** and used as an intermediate in the synthesis of certain medicinal preparations, has been obtained by treating lithium acetylcyclopropane enolate with fluorinated aryl isocyanide and subsequent hydrolytic decomposition of the intermediate adduct.[212] Finally, one should note that the reaction of acetylcyclopropane with propiolates proceeds initially as the Claisen condensation and is terminated by the cyclisation of the intermediate acetylenic diketones to γ-pyrones **88**, which are formed in moderate overall yields.[213]

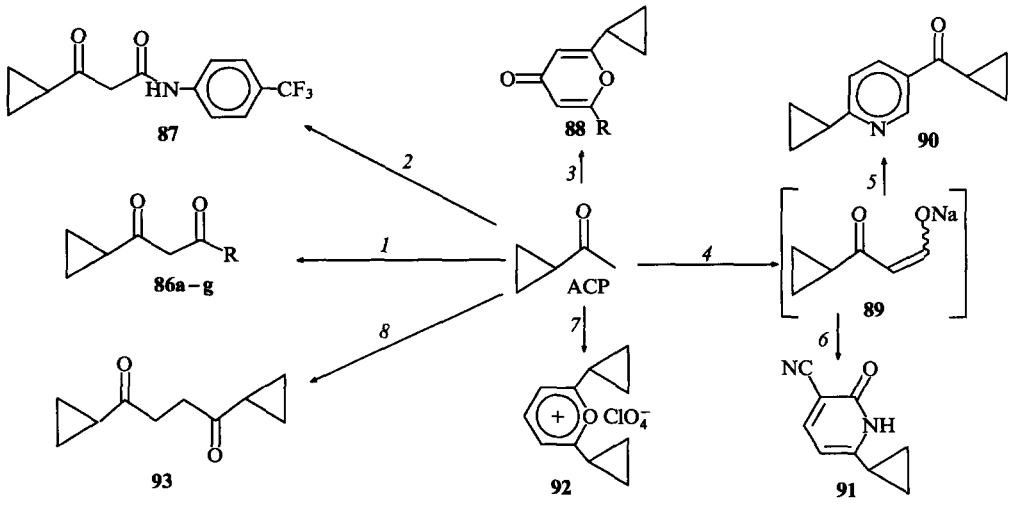
The Claisen condensation examined above, leading to the β-dicarbonyl compounds **86**, implies in the case of the formate the formation of the corresponding labile β-ketoformyl derivative. One of the interesting synthetic applications of the fairly stable sodium enolate **89**[214,215] involves its simple conversion into certain six-membered heterocycles. Thus, on treatment with ammonium acetate in acetic acid, the enolate **89** dimerises readily to the pyridine **90**[215] and reacts smoothly with cyanoacetamide in the presence of Pi.AcOH (Pi = piperidine), affording the pyridone **91**.[214] The thermal reaction of acetylcyclopropane with orthoformic ester, initiated by $HClO_4$, takes place similarly and proceeds evidently via the stage of a 1,5-dicarbonyl intermediate to the pyrylium salt **92**.[216]

In conclusion, one should note that the synthetic possibilities of enolates of type **89** as highly reactive intermediates are far from being exhausted. In particular, the lack of data on their involvement in a reaction of the Michael type and in radical-ion reactions is noteworthy. The latter apparently include the copper(II)-catalysed dimerisation of the lithium acetylcyclopropane enolate to the 1,4-diketone **93**.[217]

c. Certain reactions of activated acetylcyclopropane

Examples of the use of three readily available activated derivatives of acetylcyclopropane — the imine **18b**, the silyl ether **28**, and the hydrazone **94** — are considered below. With their aid, it is possible to achieve more effective regioselective and chemoselective reactions involving the methyl group than with the methyl ketone itself. Thus the direct chlorination of acetylcyclopropane proceeds non-selectively, affording a complex mixture of chloro-derivatives which are difficult to separate.[59] On the other hand, the ketimine **18b** reacts smoothly with *N*-chlorosuccinimide (NCS) and is converted, after the hydrolysis of the intermediate Schiff base, into the dichloroketone **95**[59] (Scheme 23).

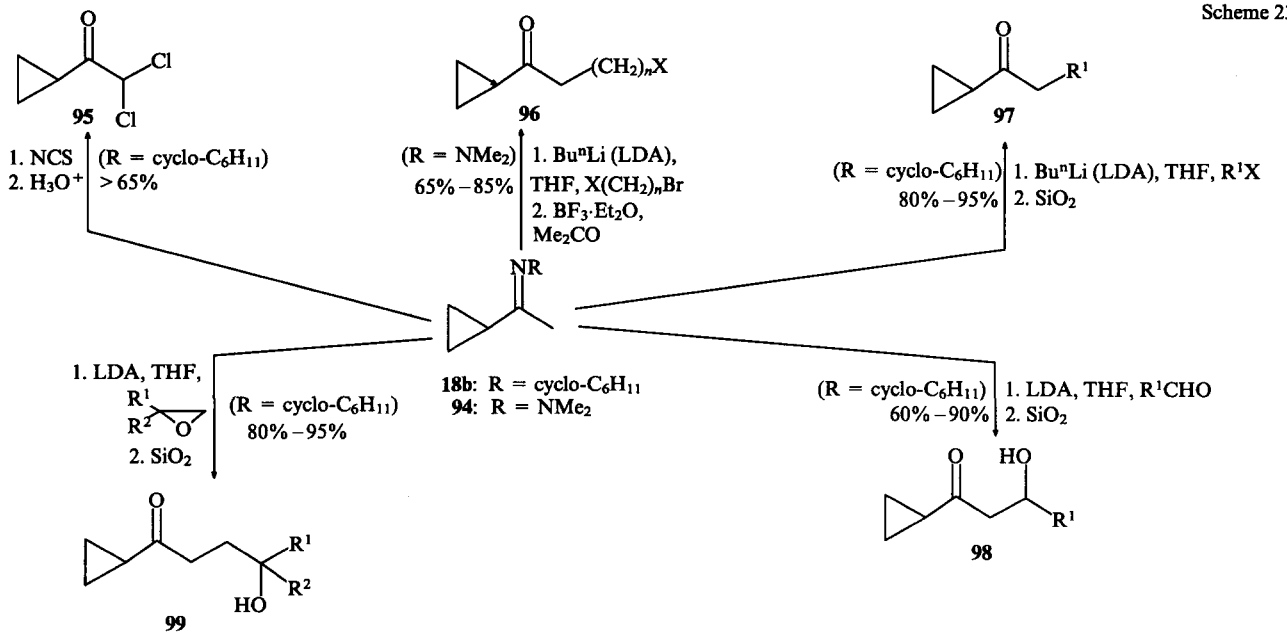
Scheme 22



88: R = H, *o*-ClC_6H_4, *p*-ClC_6H_4, *p*-$MeOC_6H_4$
86: R = Me (**a**), Et (**b**), Ph(**c**), OMe (**d**), OEt (**e**), OPh (**f**), CO_2Et (**g**)

(*1*) RCO_2R^1/BF_3 or NaH, or $NaNH_2$, or R^2ONa (20% – 85%);
(*2*) LTMP/THF, then *p*-$F_3CC_6H_4NC$, and then HCl;
(*3*) $RC{\equiv}CCO_2Et$, EtONa (25% – 60%);
(*4*) HCO_2Et, MeONa;
(*5*) AcOH, NH_4OAc (~80%);
(*6*) $NCCH_2CONH_2$, Pi·AcOH, boiling H_2O (~55%);
(*7*) $HC(OEt)_3/HClO_4$, Δ (~10%);
(*8*) LDA/CuCl, THF–DME (> 45%).

Scheme 23

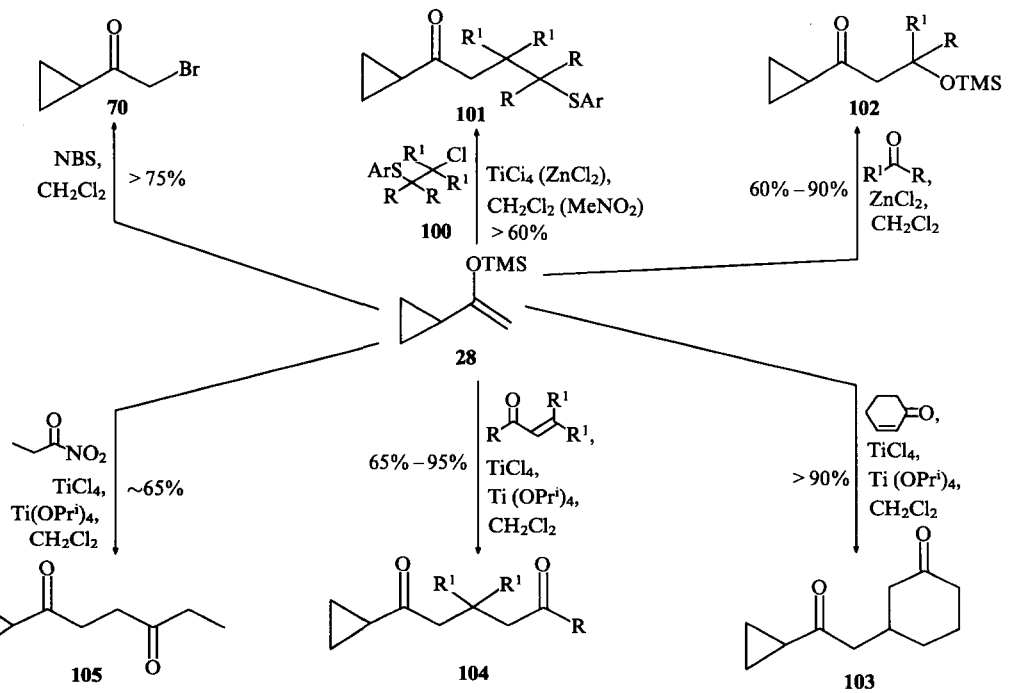


96: X = Cl, n = 3, 4; X = Br, n = 5;
97: R^1 = Me, Pr^n, n-C_7H_{15}, n-C_9H_{19}, $Me_2C{=}CHCH_2$, (*E*)-$Bu^nCH{=}CH(CH_2)_3$, (*Z*)-$Bu^nCH{=}CH(CH_2)_7$;
98: R^1 = Et, Bu^n, n-C_6H_{11}, n-C_8H_{17}, (*E*)-$MeCH{=}CH$, (*Z*)-$Bu^nCH{=}CH(CH_2)_3$;
99: R^1 = R^2 = H; R^1 = H, R^2 = Me; R^1 = Me, R^2 = $CH_2{=}CH$.

Alkylation of the products of the deprotonation of the dimethylhydrazone **94** with ω-haloalkyl bromides affords, after the hydrolytic cleavage of the corresponding adducts, the ketones **96** in high overall yields.[218] Similarly the lithio-derivative of the imine **18b** interacts readily and selectively with primary alkyl halides, aldehydes, and epoxides, affording the ketones **97**, the β-hydroxyketones **98**, and the γ-hydroxyketones **99** respectively after the hydrolysis on silica gel of the imines formed.[219–223]

Treatment of the silyl ether **28** with *N*-bromosuccinimide leads to the monobromo-derivative **70**[224] (Scheme 24) without any appreciable advantage compared with the same reaction using acetylcyclopropane itself. On the other hand, the employment of compound **28** leads to the possibility of obtaining the products of the alkylation of acetylcyclopropane by sterically very greatly hindered electrophiles of the type of vicinal arylthiochloro-derivatives **100** on treatment with Lewis acids. The γ-arylthio-substituted ketones **101** have been effectively synthesised by this method.[225,226] The interaction of aliphatic aldehydes and ketones with the silyl ether of the enol **28** is effectively catalysed by $ZnCl_2$. This reaction results in the smooth formation of β-siloxyketones

Scheme 24



101: R = H, R^1 = Me; R = CMe_2, R^1 = H;
102: R = H, R^1 = Et, Pr^i, Bu^n, n-C_6H_{11}, n-C_8H_{17}, $MeCH{=}CH$, (*E*)-$Bu^nCH{=}CH(CH_2)_2$; R = Me, R^1 = Me, cyclo-Pr;
104: R = R^1 = Me; R = Et, R^1 = H.

102, which makes it possible to solve the problem of the synthesis from acetylcyclopropane of the product of its aldol-crotonic condensation with carbonyl compounds.[227-231]

An extremely interesting synthetic application of the silyl ether **28** is based on the little investigated possibility of involving acetylcyclopropane in a reaction of the Michael type. Thus the reaction of compound **28** with conjugated ketones in the presence of mixed titanium(IV) salts leads to high yields of the 1,5-diketones **103** and **104**.[72] When nitrobutene was used as the acceptor, the 1,4-diketone **105** was obtained.[72]

Thus the large set of selective transformations of acetylcyclopropane involving its methyl group, presented in this Section, opens an extremely effective pathway to various functionalised cyclopropyl ketones, many of which are important synthons.

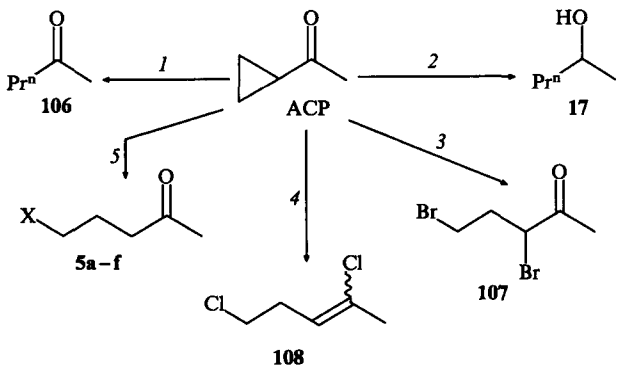
3. Reactions with participation of the cyclopropane fragment

The data examined above demonstrate the properties of acetylcyclopropane as a typical representative of aliphatic methyl ketones. The presence of the cyclopropane residue in its molecule is responsible for additional synthetic possibilities associated with the transformation of the strained three-membered carbocycle. The data described below refer to this feature of the acetylcyclopropane molecule and its derivatives and, mainly, to the ability of the corresponding secondary and tertiary amines to undergo the cyclopropylcarbinyl rearrangement (CPCR).

a. Hydrogenolysis and heterolysis of acetylcyclopropane

Catalytic hydrogenation of acetylcyclopropane leads in many instances to the initial opening of the three-membered ring and the formation of the ketone **106**, which is capable of being further reduced to the alcohol **17**[31,232-234] (Scheme 25). The maximum yield of the ketone **106** was attained when 10% Pd/C was used as the catalyst;[31,232,233] when it is replaced by the mixed Pd–Ni catalyst, the complete conversion of acetylcyclopropane into the alcohol **17** is observed.[234] The pentanone **106** has also been obtained in a high yield by the homolytic reduction of acetylcyclopropane via its photolysis or thermolysis in the presence of the $Bu^n_3SnH/AIBN$ couple (AIBN = azobisisobutyronitrile).[235-237] The Birch radical-ion reduction of acetylcyclopropane leads non-selectively to a mixture of both expected products — **17** and **106**.[34]

Scheme 25



5: X = Cl (**a**), Br (**b**), I (**c**), SPh (**d**), $P^+Ph_3Br^-$ (**e**), SePh (**f**)

(*1*) H_2/Cu, 80 °C (~20%), H_2/Pd–C (90%), $Bu^n_3SnH/AIBN/h\nu(\Delta)$(85%), Na/NH_3 (in a mixture with compound **17**);
(*2*) H_2/Cu, 125 °C (55%), H_2/Pd–Ni (> 90%);
(*3*) Br_2/CH_2Cl_2 ($CHCl_3$, AcOH) (~30%);
(*4*) PCl_5/boiling CH_2Cl_2;
(*5*) Py·HCl (> 80%), P_2I_4 (~90%), Me_3SiX (X = Cl, Br, I) (85% – 95%), $AlCl_3$/PhSH (Me_3SiSPh) (35% – 45%); Ph_3P·HBr (> 90%), PhSeLi (90%).

The results of the hitherto little investigated interaction of various cationoid reagents with acetylcyclopropane may be of great synthetic interest. The electron-accepting nature of the acetyl residue of acetylcyclopropane induces via an inductive mechanism the polarisation of the C–C 'banana' bond,[238] as a result of which this molecule resembles to some extent electrophilic olefins. The competition (evidently in favour of the C=O group) between the intermolecular and intramolecular coordination of the electrophile to the acetylcyclopropane molecule should promote additional polarisation of the above bond and hence an increase in the reactivity of the cyclopropane fragment.

In conformity with the foregoing considerations, the bromination of acetylcyclopropane in chlorinated hydrocarbons leads to a moderate yield of the acyclic dibromo-derivative **107**.[239,240] When the reaction is carried out in acetic acid, its effectiveness is not significantly affected but it becomes complicated by a competing process leading to the formation of appreciable amounts of γ-bromoketone **5b**.[240] Taking into account the data examined above in the synthesis of the α-bromoketone **70**, the data discussed here may serve as a good illustration of the influence of the polarity of the medium on the result of the electrophilic reaction in relation to a chemically fairly simple substrate. The conversion of acetylcyclopropane into a mixture of (*E*)- and (*Z*)-dichloro-derivatives **108** under the influence of PCl_5 in boiling CH_2Cl_2 may be referred to the same type of reactions.[241]

Data obtained recently on the interaction of acetylcyclopropane with soft acids may have significantly more important synthetic consequences. Thus the γ-chloroketone **5a** is formed smoothly when acetylcyclopropane is treated with pyridinium chloride.[242,243] There is no information about a similar reaction with pyridinium bromide, although it is known that in the case of the related pyridinium iodide, which has reducing properties, a complex mixture of substances of unknown structure is produced.[243] However, the γ-iodoketone **5c** can be obtained in a high yield by treating acetylcyclopropane with P_2I_4 under mild conditions.[244]

The use of available or generated *in situ* trimethylsilyl halides is a universal and effective procedure for transforming acetylcyclopropane into the γ-haloketones **5a–c**,[245,246] with *O*-silyl ethers as reaction intermediates. The $AlCl_3$-catalysed effective transformation of acetylcyclopropane into the γ-phenylthioalkyl ketone **5d** on treatment with thiophenol or its trimethylsilyl derivative[246] and the synthesis of the phosphonium salt **5e** on treatment of acetylcyclopropane with PPh_3·HBr have been achieved in conformity with the same principle.[247]

In conclusion of this Section, the absence of data on the anionoid opening of the acetylcyclopropane ring and hence on its involvement in a series of synthetically useful transformations should be noted. So far the effective conversion of acetylcyclopropane into the ketoselenide **5f** on treatment with PhSeLi may serve as the only example of this kind.[248]

b. The cyclopropylcarbinyl rearrangement

The data discussed below refer to the chemistry of secondary and tertiary cyclopropylcarbinols, readily obtainable from acetylcyclopropane, which have recently found extensive applications by virtue of their unique ability to undergo the cyclopropylcarbinyl rearrangement on treatment with protic and Lewis acids.[249-251] It is now well known that such rearrangement of secondary alcohols takes place highly stereoselectively, affording as a rule, high yields of the corresponding (*E*)-olefins. Thus cyclopropylmethylcarbinol **16** readily isomerises under the conditions of the Julia reaction (48% HBr) to the homoallyl bromide **110a**[35,36,38-40] (Scheme 26). A similar transformation can be readily achieved with the aid of $MgBr_2$ and this approach has proved extremely effective also for the preparation of the iodide **110b** from compound **16** on treatment with MgI_2.[112] Another version of the transformation of cyclopropylcarbinols into homoallyl iodides involves the use of 40% HI in DME (dimethoxyethane?). This method was applied to the synthesis

of the anisyl derivative **111** from the alcohol **109a** prepared by the two-stage reduction of the enone **83e** (R = *m*-$MeOC_6H_4$).[182] The conversion of the alcohol **109b**, obtained from the ketoester **86e**, into the bromoester **112** has been achieved successfully on treatment with a solution of $ZnBr_2$ in 48% HBr.[211,252] It was shown recently that the cyclopropylcarbinyl rearrangement of the saturated (compounds **109c–i**) and allylic (compounds **114a–f**) cyclopropylcarbinols obtained from acetylcyclopropane takes place readily under mild conditions under the influence of trimethyl silyl halides and catalytic amounts of zinc halides, affording the corresponding (*E*)-homoallyl halides **113a–i** and **115a–i** in high yields.[219–223,227–231] The method makes it possible to obtain equally effectively both the bromides **113c–i** and **115e–i** and the chlorides **113a, b** and **115a–d**. In contrast to the saturated alcohols, the allyl alcohols **114** are capable of rearranging with the aid of HCO_2H and AcOH to the transoid homoallyl formates and acetates of the type **116a, b** and **116c, d** respectively.[253]

Numerous tertiary cyclopropylmethylcarbinols **49**, readily obtained in one stage from acetylcyclopropane, have been involved in the classical Julia reaction with the use of 48% HBr (Scheme 27). In contrast to the secondary carbinols, tertiary cyclopropylcarbinols afford under these conditions as a rule mixtures of (*E*)- and (*Z*)-stereoisomeric bromides **117** in different proportions, mainly with one of them predominating. The ethynylcarbinols **49u, v** are an exception. Their Julia conversion under the conditions indicated leads almost wholly to the (*Z*)-isomers **117u, v**,[129,131] which has been used successfully in one of the simple schemes for the total synthesis of the juvenile hormone I.[256] There is as yet no rational explanation of this unique steric effect, although in purely qualitative terms it may reduce to the fact that the conformation of the transition state in the rearrangement is determined by the minimum overlap of the cyclopropyl substituent with the methyl substituent, which is significantly more bulky than the ethynyl substituent.[129]

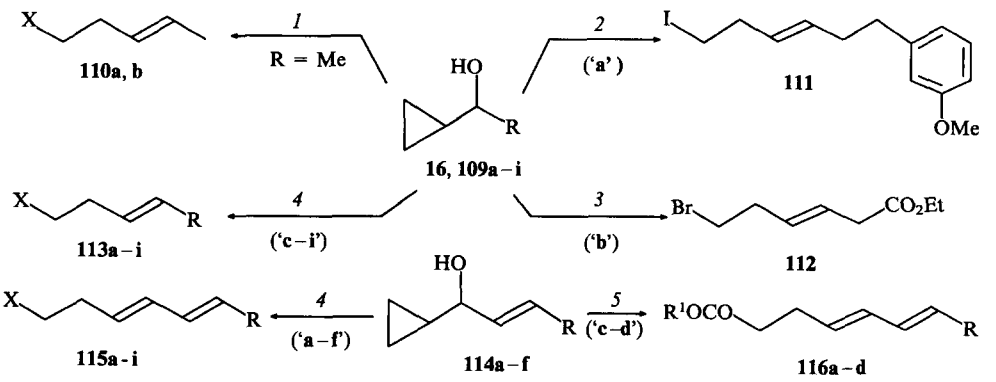
The homoallyl bromides **117**, which are stereochemically inhomogeneous as regards the trisubstituted C=C bond, have nevertheless found practical applications in the synthesis of various natural products, predominantly of the isoprenoid series.

The cyclopropylcarbinyl rearrangement of alcohols **49** proceeds almost always with high yields and without complications and for this reason only certain features of this reaction are noted below. Thus the formation of up to 14% of the olefin hydrobromination product **117a** has been noted in the isomerisation of compound **49a**.[111] The conversion of the homoallyl alcohol **49k** is partly (~15%) accompanied by a shift of the terminal double bond of the product **117k** with formation of a conjugated diene.[131]

Scheme 28 presents other versions of the procedure for carrying out the cyclopropylcarbinyl rearrangement of tertiary carbinols **49** different from that in the standard Julia method. Thus the unusual LiBr/TsOH/AcOH/Ac_2O system has been used to obtain the 3,5-dienyl bromide **117h** without explanation of its advantage over 48% HBr.[130] As in the case of secondary cyclopropylcarbinols, the tertiary carbinols rearrange smoothly and almost quantitatively under the influence of $MgBr_2$ and MgI_2 to the corresponding homoallyl halides **117** with the (*E*)-isomer predominating in the case of compound **117b**.[112]

The use of aqueous HCl to convert cyclopropylcarbinol into homoallyl chlorides is characterised by the absence of regioselectivity. Thus in the four instances of this reaction, only one, leading to the homoprenyl chloride **118a**, can be regarded as unambiguous.[106] Apart from the expected olefins **118e, r, u**, in the remaining three cases the corresponding dienes and their hydrochlorination products as well as the corresponding cyclobutyl chlorides were detected.[124,139,258]

Scheme 26



16: R = Me;

109: R = *m*-$MeOC_6H_4(CH_2)_2$ (**a**), CH_2CO_2Et (**b**), Et (**c**), Bu^n (**d**), n-C_8H_{17} (**e**), n-$C_{10}H_{21}$ (**f**), (*E*)-$Bu^nCH=CH(CH_2)_4$ (**g**), (*Z*)-$Bu^nCH=CH(CH_2)_8$ (**h**), $HO(CH_2)_3$ (**i**);

110: X = Br (**a**), I (**b**);
X = Cl: R = Bu^n (**a**), n-C_8H_{17} (**b**);
X = Br: R = Et (**c**), Bu^n (**d**), n-C_8H_{17} (**e**), n-$C_{10}H_{21}$ (**f**), (*E*)-$Bu^nCH=CH(CH_2)_4$ (**g**), (*Z*)-$Bu^nCH=CH(CH_2)_8$ (**h**), $HO(CH_2)_3$ (**i**);

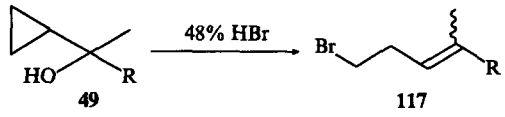
114: R = Et (**a**), Pr^i (**b**), Bu^n (**c**), n-C_8H_{17} (**d**), (*E*)-MeCH=CH (**e**), (*Z*)-$Bu^nCH=CH(CH_2)_3$ (**f**);

115: X = Cl: R = Pr^i (**a**), Bu^n (**b**), n-C_8H_{17} (**c**), (*E*)-MeCH=CH (**d**);
X = Br: R = Et (**e**), Pr^i (**f**), Bu^n (**g**), n-C_8H_{17} (**h**), (*Z*)-$Bu^nCH=CH(CH_2)_3$ (**i**);

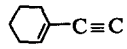
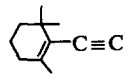
116: R^1 = H: R = Bu^n (**a**), n-C_8H_{17} (**b**);
R^1 = Me: R = Bu^n (**c**), n-C_8H_{17} (**d**);

(*1*) 48% HBr (> 80%), Et_2O·MgX (70% – 90%);
(*2*) 40% HI–DME (75%);
(*3*) 48% HBr/$ZnBr_2$;
(*4*) Me_3SiX/ZnX_2, CH_2Cl_2 (65% – 100%);
(*5*) R^1CO_2H (60% – 90%).

Scheme 27



49 117

No.	R	*E*/*Z*	Yield of **117** (%)	Ref.
a	Me	–	75	110, 111, 115
b	Et	3:1	98	117, 118
c	Pr^n	5:2	79	120–122
g	$HO(CH_2)_4$	[a]	87	127
h	$CH_2=CH$	3:1	85	128, 129, 254, 255
i	(*Z*)-MeCH=CH	3:2	90	131
k	$CH_2=CHCH_2$	4:1	78	131–133
l	(*E*)-MeCH=CH$(CH_2)_2$	7:1	67	135
m	EtMeC=CH$(CH_2)_2$	[a]	70	136
o	$Pent^i$MeC=CH$(CH_2)_2$	[a]	75	136
p	$H(CH_2CMe=CHCH_2)_nCH_2$			
	$n=1$	[a]	83	110, 111, 129, 132, 136
	$n=2$	[a]	84	110, 111, 132, 136
	$n=3$	[a]	61	111
s	Bn	5:1	85	142
u	HC≡C	1:19	88	128, 129, 144, 145, 256
v	MeC≡C	1:16	90	131, 257
x		[a]	98	150
y		[a]	96	150
b'	HC≡CCH_2	4:1	87	131
e'	EtO_2CCH_2	[a]	78	160

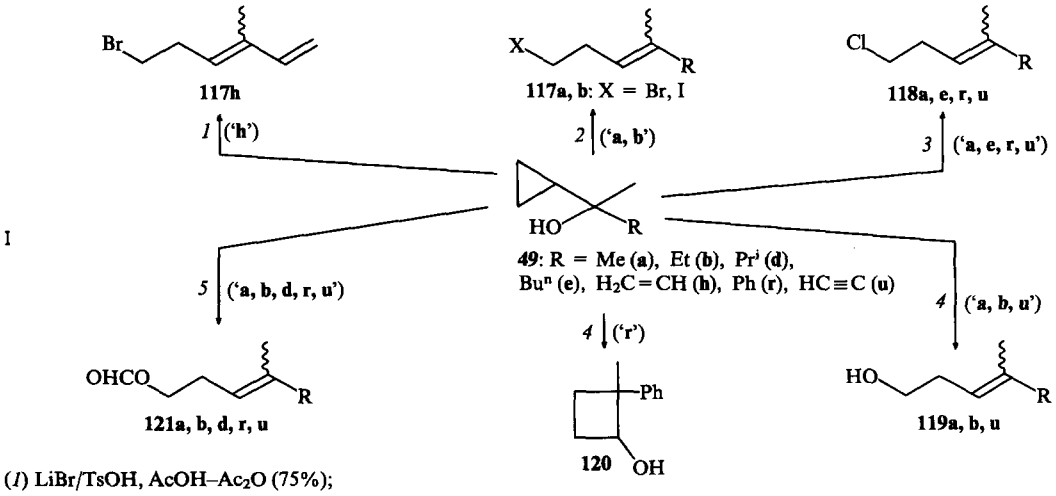
[a] Data on the isomeric composition are not available.

Extremely varied products were obtained when aqueous H_2SO_4 was used for the cyclopropylcarbinyl rearrangement of tertiary alcohols. For example, in the case of compounds **49a, b, u**, mixtures of the homoallyl alcohols **119a, b, u**, together with the products of their dehydration, intramolecular cyclisation, and dimerisation were isolated in low yields.[109,139,147] Under the same conditions, the benzyl alcohol **49r** is converted predominantly into cyclobutanol **120**.[139]

The selectivity of the isomerisation of tertiary cyclopropylcarbinols under the influence of HCO_2H depends to a significant extent on the conditions in this reaction. Thus heating of compounds **49a, b, r, u** with 20%–50% aqueous solutions of HCO_2H affords a complex mixture of substances with a low content of the formates **121a, b, r, u**.[108,116,140,258] On the other hand, the use of 98% HCO_2H in THF leads smoothly to the formates **121a, b, d**.[259,260]

A successful modification of the two-stage synthesis, examined above, of homoallyl halides from cyclopropyl ketones via a stage involving tertiary carbinols consists in the treatment with 50% H_2SO_4 of the alkoxide formed in the reaction between a Grignard reagent and acetylcyclopropane (Scheme 29).

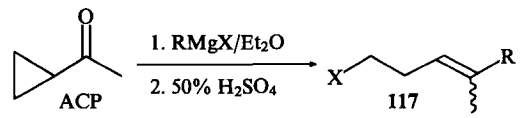
Scheme 28



I

(*1*) LiBr/TsOH, AcOH–Ac_2O (75%);
(*2*) $Et_2O{\cdot}MgX_2$ (~100%);
(*3*) 20%–36% HCl (45%–75%);
(*4*) 10%–50% H_2SO_4 (25%–45%);
(*5*) 20%–98% HCO_2H (40%–60%).

Scheme 29

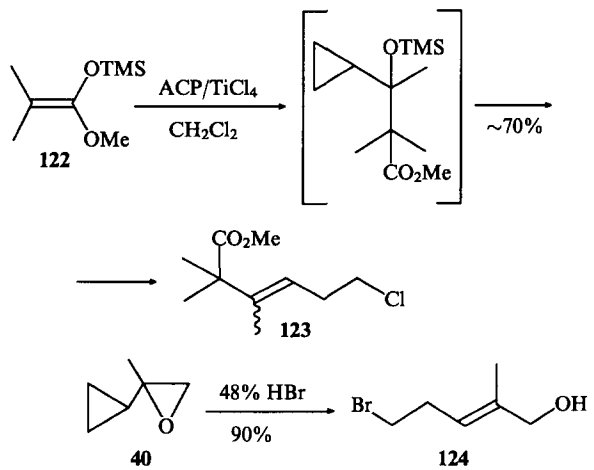


No.	R	X	E/Z	Yield of 117 (%)	Ref.
a	Me	Br	–	88	261
e	Bu^n	Br	4:1	60	262
m	$EtMeC=CH(CH_2)_2$	Br	[a]	62	136
n	$Bu^nMeC=CH(CH_2)_2$	Br	[a]	67	262
o	$Pent^iMeC=CH(CH_2)_2$	Br	7:2	46	136
p	$H(CH_2CMe=CHCH_2)_nCH_2$				
	$n=1$	Br	[a]	77	136
	$n=2$	Br	3:1	60	136
r	$EtMeC=CH(CH_2)_2$	I	[a]	62	136
t	$Pent^iMeC=CH(CH_2)_2$	I	3:1	49	136
w	$H(CH_2CMe=CHCH_2)_nCH_2$				
	$n=1$	I	7:2	72	136, 263
	$n=2$	I	7:2	41	136
z	$MeOCHMe(CH_2)_3$	Cl	3:1	61	264

[a] Data on the isomeric composition are not available.

A large number of halides **117**, used in the synthesis of pheromones, juvenile hormones, and other biologically active substances, have been synthesised by this single-stage method. Yet another example of the cyclopropylcarbinyl rearrangement without the isolation of the intermediate tertiary alcohol consists in the $TiCl_4$-initiated condensation of acetylcyclopropane with the ketene acetal **122**, which leads smoothly to a mixture of the stereoisomeric homoallyl chlorides **123** (Scheme 30).[265]

Scheme 30

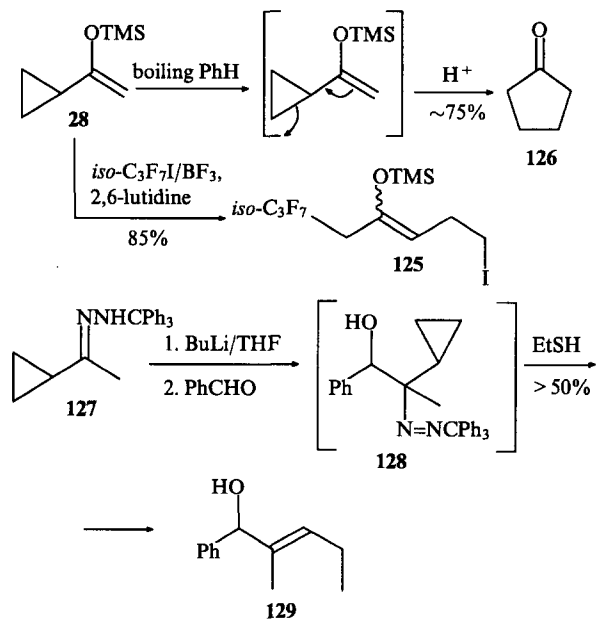


In conclusion, mention should be made of the isomerisation of the epoxide **40**, which takes place in accordance with the mechanism of the cyclopropylcarbinyl rearrangement under the influence of 48% HBr and is distinguished by a high stereoselectivity [> 96% of the (*E*)-isomer] and affords an almost quantitative yield of the bromohydrin **124**.[93]

c. Other reactions with participation of the three-membered ring

Individual examples of the involvement of certain derivatives of acetylcyclopropane in reactions via the carbonyl group, which proceed formally with participation of the acetyl and cyclopropane fragments of this molecule, have been described. Thus, treatment of the trimethylsilyl ether **28** with perfluoroisopropyl iodide in the presence of a base and BF_3 leads selectively to a mixture of the isomeric siloxyiodo-derivatives **125** ($Z:E$ = 4:1)[266] (Scheme 31). The reaction apparently proceeds via a radical ion mechanism involving the cyclopropyl-carbinyl rearrangement at an intermediate stage.

Scheme 31



The thermolysis of the enolate **28** induces its rearrangement with ring expansion and the formation of the cyclopentanone **126** in a high yield after the hydrolysis of the intermediate trimethylsilyl ether.[76]

The deprotonation and subsequent treatment with benzaldehyde of the hydrazone **127**, readily obtainable from acetylcyclopropane, afford the intermediate azo-compound **128**, which undergoes under mild conditions the radical homoallyl rearrangement to the (*E*)-olefin **129** with a stereochemical purity of 93%.[52]

Thus the reactions of acetylcyclopropane and its derivatives with participation of the three-membered ring permit convenient and in many instances the most rational synthesis of various acyclic functionalised compounds, including ketones and saturated and unsaturated halides and alcohols.

IV. The use of acetylcyclopropane in the synthesis of natural and practically useful compounds

Some of the reactions of acetylcyclopropane examined above served as a basis for a series of schemes for the specific synthesis of pheromones, terpenoids, steroids, vitamins, prostanoids, alkaloids, as well as medicinal preparations and herbicides.

1. Synthesis of acetogenin pheromones

The use of acetylcyclopropane as the five-carbon (*E*)-fragment served as the basis for the stereoselective synthesis of a whole series of acetogenin transoid pheromones of the insects of the order Lepidoptera. The pheromones, having the structure of (*E*)-homoallyl acetates **130–132**, were obtained in one stage and in high yields from the corresponding bromides **113e, h** and **115h** (Scheme 32).[222,228,229,267]

The synthesis of a large number of other acetogenin pheromones, including alkene (**133**[219–221,223,231,267]), diene (**134**[220,267] and **135**[39,221,223]), as well as triene (**136**[221,222]) representatives has been achieved with the aid of various methods for increasing the length of the carbon–carbon linear chain in the homoallyl halides **110a, 113c, d, i,** and **115b, e, i** (Scheme 33).

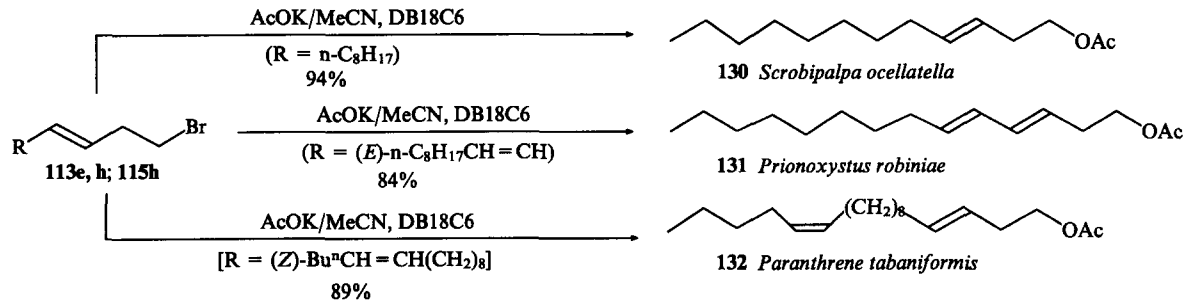
2. Synthesis of terpenoids

The method developed by Julia for the synthesis of homoallyl bromides has served as a key procedure in the synthesis of acyclic terpenoids based on acetylcyclopropane.[35,115,117,120–122,135,145,150,160,256,257,261–264,268]

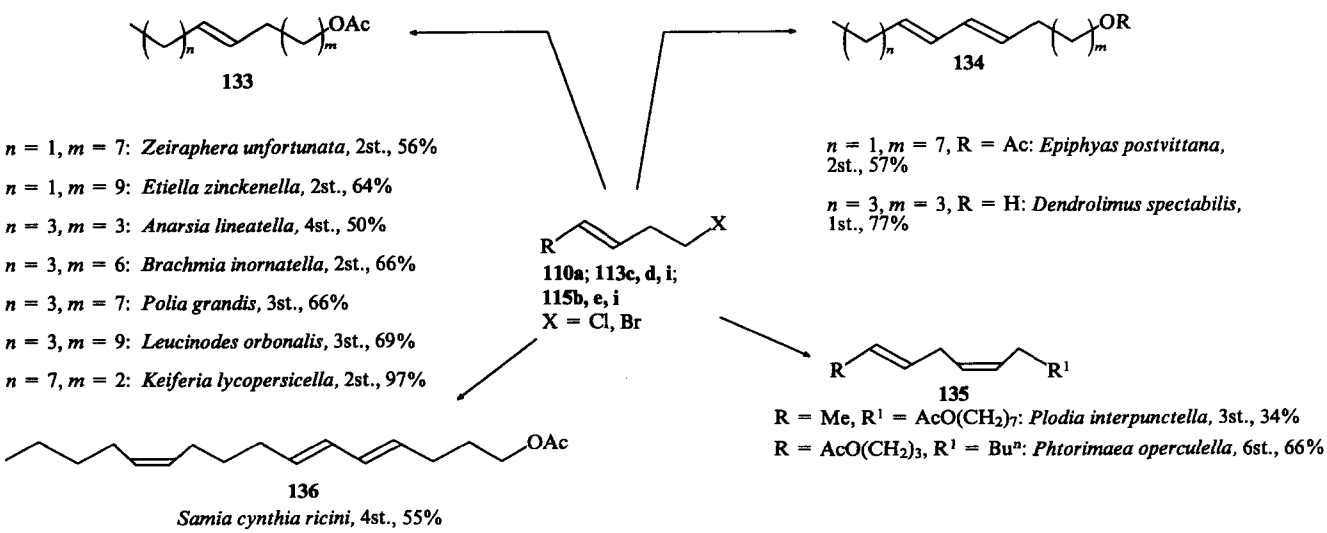
One of the simplest syntheses of linalool **137** includes the metallation of the bromide **117a** and subsequent condensation of the resulting lithio-derivative with methyl vinyl ketone[11] (Scheme 34). In many cases, acetylcyclopropane is introduced into a Grignard reaction with the homoallyl bromide prepared from it; repetition of this operation ensures the successive growth of the linear isoprenoid chain.[110,111,129,132,133,137,262] This simple procedure has been used, in particular, for the synthesis of the (*E*)- and (*Z*)-isomers of homogeraniol **138** (*n* = 1) and homofarnesol **138** (*n* = 2) by the reaction of the Grignard reagents obtained from the bromides **117a** and **117p** (*n* = 1) with acetylcyclopropane and the subsequent cyclopropylcarbinyl rearrangement of the cyclopropylcarbinols formed. The conversion of the bromide **117p** into the corresponding alcohols **138** was carried out by their standard acetolysis and the hydrolysis of the acetates in the final stage.[111]

It is noteworthy that the advantages of this universal method are partly abolished by the absence, already mentioned above, of the stereoselectivity in the rearrangement of the tertiary cyclopropylcarbinols. The syntheses of the racemates of saturated isoprenoids based on acetylcyclopropane are free from this disadvantage.[118,121,122,211,252,262] Thus (±)-5,9-dimethylheptadecane **139**, which is the sex pheromone of the apple leafminer moth *Leucoptera malifoliella*, has been obtained by the cross-coupling of the homoallyl bromide **117n** with pentylmagnesium bromide in the presence of the Cauchy reagent [sic. lithium copper chloride in original paper. (Translator)] and the subsequent hydrogenation of the resulting diene.[262] The bromide **117n** was synthesised for this purpose from acetylcyclopropane and Bu^nMgBr via its C_5-norhomologue **117e** involving two applications of the cyclopropylcarbinyl rearrangement.

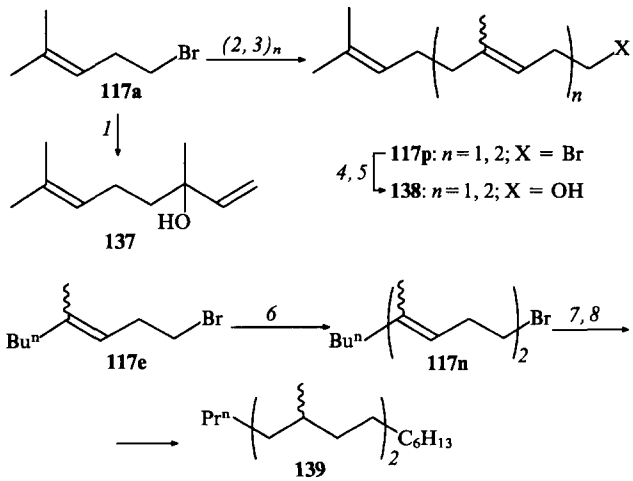
Scheme 32



Scheme 33



Scheme 34



(*1*) Li/Et_2O, then $MeC(O)CH{=}CH_2$ (~20%);
(*2*) Mg, then ACP (55% – 80%);
(*3*) 48% HBr (~80%);
(*4*) AcOK/AcOH;
(*5*) K_2CO_3/MeOH (~75% from **117p**);
(*6*) Mg, then ACP, then 50% H_2SO_4 (~70%);
(*7*) Pe^nMgBr, Li_2CuCl_4/THF;
(*8*) H_2/Pd–C (85% from **117n**).

3. Conversion into steroids, vitamins, and a prostanoid synthon

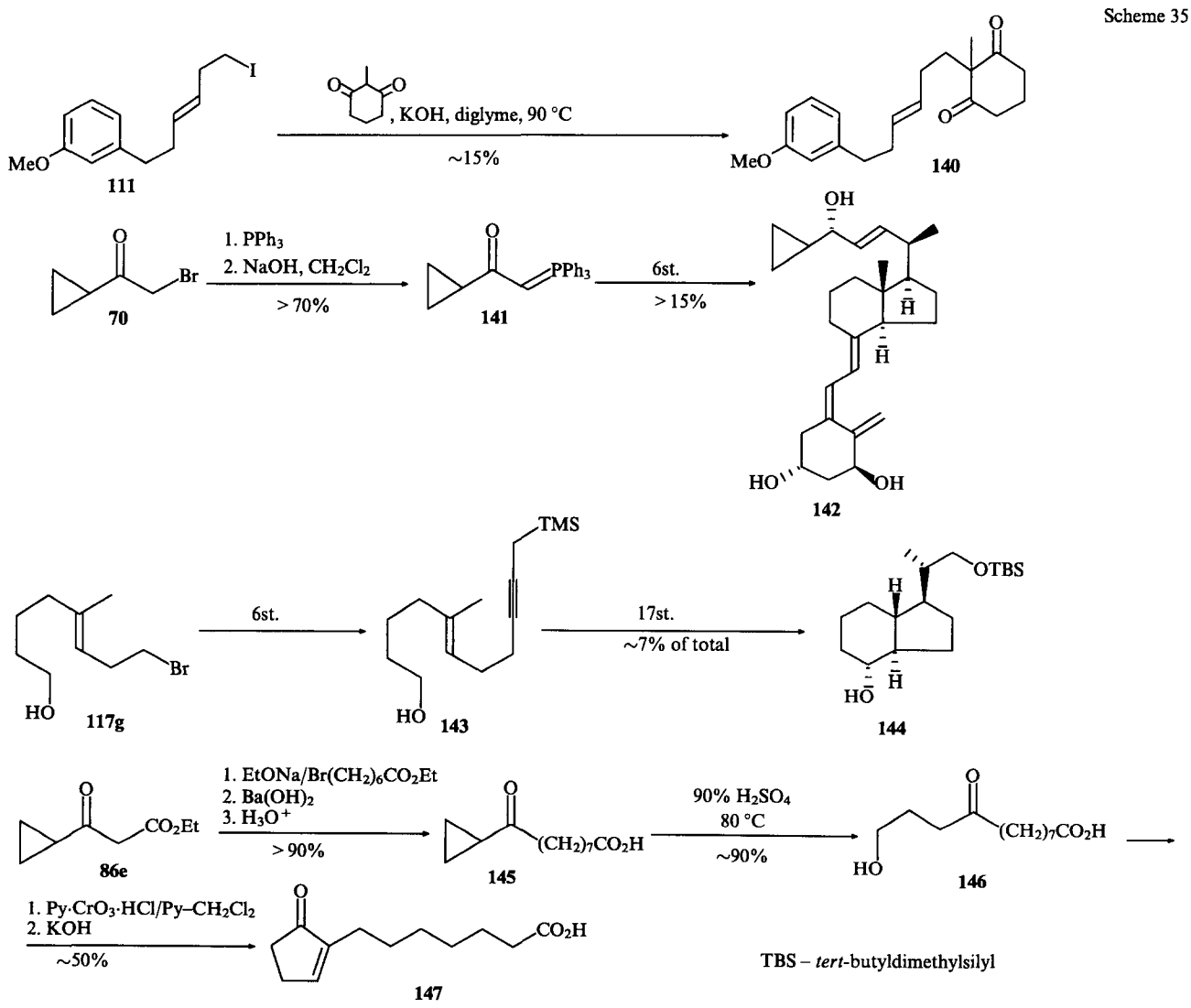
The homoallyl iodide **111**, prepared in three stages from acetylcyclopropane, has been used in the synthesis of D-homodehydrooestranes by Torgov's method. The key stage in this process is the alkylation by the iodide **111** of 2-methylcyclohexane-1,3-dione with formation of the diketone **140** (Scheme 35).[182]

The cyclopropyl analogue of vitamin B **142**, which exhibits a high physiological activity,has been synthesised using in one of the stages the phosphorane **141** prepared from the bromoketone **70**.[184]

The key intermediate **144** in the synthesis of vitamin D_3 was obtained in 25 stages from acetylcyclopropane.[127] The main strategy reduces in this case to the formation in the early stages of the functionalised *trans*-perhydroindan skeleton, which is achieved on the basis of the unsaturated silane **143**, prepared in its turn from the available homallyl bromide **117g**.

The increase in the length of the ketoester **86e** by a six-carbon fragment and the subsequent hydrolytic opening of the cyclopropane residue in the ketone **145** by heating it with concentrated H_2SO_4 lead to the ketol **146**, which is converted by the oxidation and intramolecular condensation of the intermediate ketoaldehyde into the cyclopentenone **147** — a widely used prostanoid synthon.[210]

Scheme 35

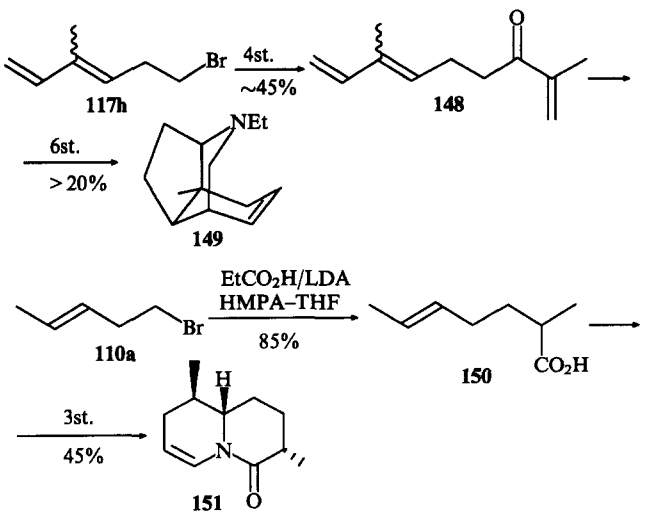


TBS – *tert*-butyldimethylsilyl

4. Synthesis of alkaloid fragments

Acetylcyclopropane has served as the starting compound in the model syntheses of the hexacyclic diterpene alkaloids of the aconitine series and also of tricyclic sesquiterpene alkaloids of the nupharidine type. In the first case, the increase in the length of the carbon chains of the homoallyl bromides **117h** afforded the key trienones **148**, transformed subsequently into the tricyclic aminoalkene **149** (Scheme 36).[254,255] In the second case, alkylation of the dilithio-derivative of propionic acid with the bromide **110a**, readily obtained from acetylcyclopropane, led to the unsaturated acid **150**, which is a key intermediate for conversion into the quinolizidinone **151**.[38]

Scheme 36



5. Synthesis of medicinal preparations and herbicides

A whole series of substances of practical importance have been synthesised from acetylcyclopropane (Schemes 37 and 38).

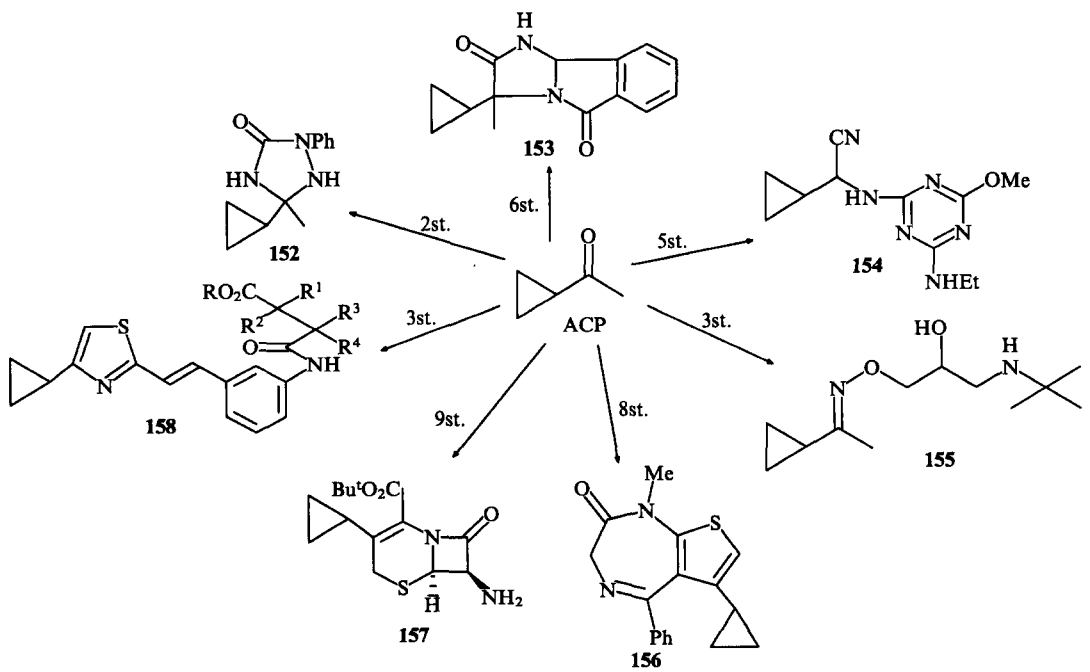
In the first stages of the syntheses of each of compounds **152–164**, the transformations of acetylcyclopropane discussed above were employed. The intermediates used in the syntheses were as follows: acetylcyclopropane hydrazone for the synthesis of compound **152**;[49] the aminonitrile **22** for the syntheses of compounds **153**[56] and **154**;[55] acetylcyclopropane oxime for the synthesis of compound **155**;[46] the vinylnitrile **44b** for the synthesis of compound **156**;[96] the bromoketone **70** for the syntheses of compounds **157**[224] and **158**;[185] the alkoxydiketones **86d, e** for the syntheses of compounds **159a, b**[208] and **160a, b**;[209] the ketoamide **87** for the synthesis of compound **161**;[212] the ketone **83e** for the syntheses of compounds **162**,[205,206] **163**,[203] and **164**.[199]

A high herbicidal activity was found in the polynitrogen heterocyclic representatives **152–154** while the ketoxime **155** was found to possess antiglaucoma activity. The diazepinone **156** exhibits pronounced antitumour properties,. while the azetidinone **157** has bactericidal properties. The thiazole derivatives **158** were found to have antiallergic activity, while the enaminoketones **159a, b** and the isoxazoles **160a, b** showed an analgesic activity. The fluorine-containing isoxazole **161** is recommended as a powerful antiarthritic drug, while the oxazole **162** is recommended as an antiviral agent. Finally, anti-inflammatory properties were found in a derivative of the aminoalcohol **163**, while the substituted pyrrolidines **164** were found to lead to the loss of appetite in dogs.

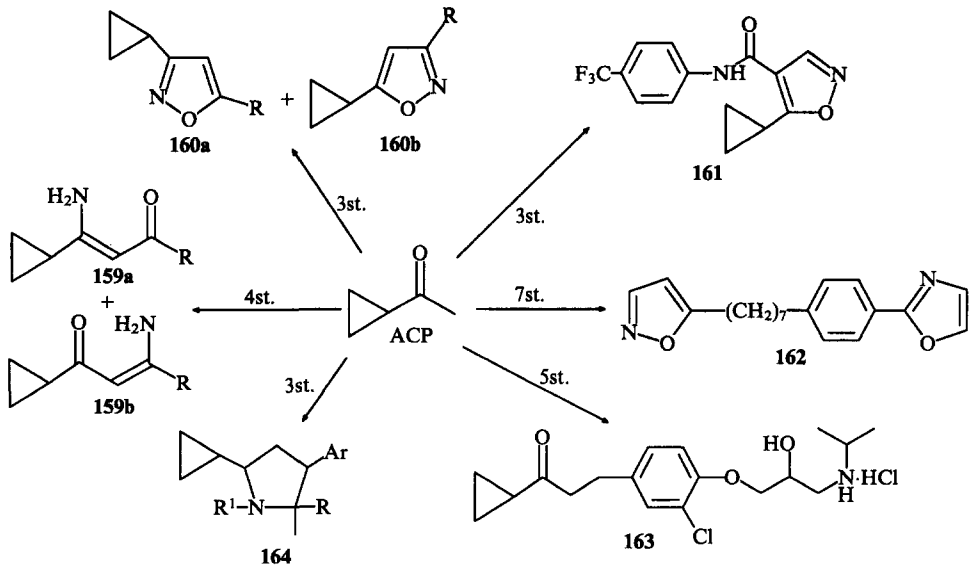
It is noteworthy that all the compounds examined above, with the exception of compound **162**, contain in their structure a three-membered ring, which is transferred from the initial acetylcyclopropane molecule.

The data described in this review illustrate the abundance of the chemical reactions of acetylcyclopropane, characteristic not only of methyl ketones but also of cyclopropylcarbinol derivatives. The possibilities in the selective transformations of acetylcyclopropane with participation of the methyl, carbonyl, or cyclopropyl groups serve as a basis for the extensive synthetic use of this commercially readily available C_5 building block. There is no doubt that this application will develop vigorously.

Scheme 37



Scheme 38



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