Reviews

New chlorinated cyclopentenones prepared from hexachlorocyclopentadiene: synthesis, chemical properties, and application in the synthesis

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The review surveys chemical conversions of 5-substituted 2,3,5-trichloro-4,4-dimethoxycyclopent-2-en-1-ones and related compounds and the possibilities of their use in the synthesis.

Key words: hexachlorocyclopentadiene, alkoxides of alcohols, tandem conversions, trichlorocyclopentenones, reactions, biologically active cyclopentanoids.

The large-scale production of hexachlorocyclopentadiene (HCCPD) involves exhaustive chlorination of cyclopentadiene. Previously,[1—3] hexachlorocyclopentadiene has been used in the production of chlorinated cage compounds (Diels—Alder adducts), which found application as antipyrenes, herbicides, fungicides, insecticides, *etc*. Recently, the production of some pesticides, in particular, of aldrine, dildrin, endosulfane, *etc.,* was virtually ceased for ecological reasons because of their low natural degradation and formation of toxic perchlorinated compounds.[4] However, studies on the construction of nonflammable substances and other materials possessing specific properties based on HCCPD[5] are still of practical importance and have considerable promise.

It is known[6,7] that HCCPD was the first diene involved in Diels—Alder reactions that shows the reverse electronic character with respect to a dienophile. Hexachlorocyclopentadiene readily forms the aromatic pentachlorocyclopentadienylium anion. Investigations in this field contributed to the development of the concept of X-philic reactions in organic chemistry.[8]

Transformed HCCPD derivatives, *viz.*, 1,2,3,4-tetrachlorocyclopentadiene, various chlorine-containing cyclopentenediones, cyclopentane-1,3-dione, and 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene, are actively used in the fine organic synthesis. The latter compound proved to be highly reactive in the dienic synthesis and enters into the [4+2] cycloaddition even with dienophiles, which are nonreactive in such reactions. This offered a convenient approach to functionalized norbornene derivatives, which have been previously difficultly accessible. Based on these derivatives, a series of natural compounds were synthesized[9,10] (coronofacic acid, cuparenone, and steroids). Cyclopentane-1,3-dione derivatives are used in the synthesis of steroids and other low-molecular-weight biological regulators.[11]

Known sequences of HCCPD transformations giving rise to compounds with useful properties are rather simple and apparent. These conversions of HCCPD can formally be characterized as reactions proceeding either with retention of Cl atoms (pesticides, antipyrenes) or with complete removal of Cl atoms by one-stage reductive dechlorination of Diels—Alder adducts (syntheses

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of natural compounds). At the same time, HCCPD, which contains Cl atoms exhibiting different reactivities, a closed system of conjugated π bonds, and activated allylic positions and which possesses other characteristic structural features, is, in our opinion, a promising compound for the search for original transformations, which can provide the basis for new approaches to cyclopentanoids.

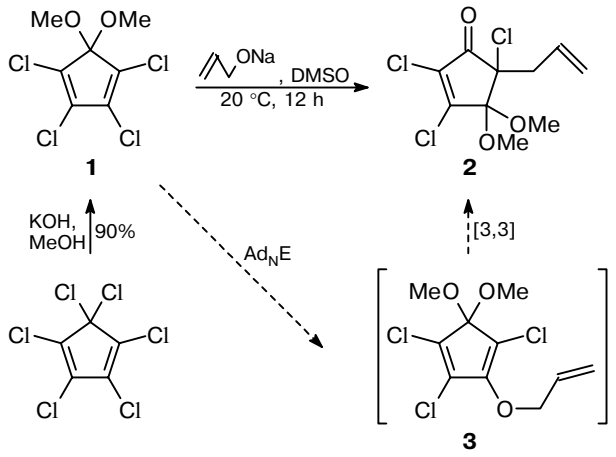
Hexachlorocyclopentadiene attracted our attention as a possible starting compound for the synthesis of biologically active substances of the cylcopentane series, in particular, once new reactions of HCCPD with anions of allylic, benzylic, propargylic, and other alcohols have been developed[12] and the approach to 5-R-2,3,5-trichloro-4,4-dimethoxycyclopent-2-en-1-ones has been devised. The resulting cyclopentenones are saturated with reactive functional groups and substituents. These compounds can be involved in diversified reactions and they will, evidently, find wide use in the organic synthesis.

In addition, the interest in chlorinated cyclopentenones stems from their biological activities. It is known that compounds containing the cyclopentenone and alkylidenecyclopentenone fragments are numerous and belong to various classes of natural substances (prostaglandins A and J, dicranenones, preclavulone A, sarcomycin, quadrone, forbol, *etc.*). The profile of biological activity (antibiotic, antiviral, and antitumor properties) of the above-mentioned compounds is determined by the fragment of α,β-unsaturated ketone, capable of being covalently bound to the SH or NH_2 functional groups of biological systems through the Michael reaction. Of particular interest are biologically active natural compounds analogous to those described above, which contain the electron-withdrawing chlorine atom in the cyclic enone fragment of the molecule (cryptosporiopsin,[13] chlorovulones,[14] and punaglandins[15]). Obviously, the presence of the chlorine atom enhances the chemical property of the molecule as a Michael acceptor, which, in turn, leads to an increase in its biological activity. All the aforesaid gave impetus to our systematic research into the chemistry of chlorinated cyclopentenones. In the last decade, we performed a large body of research and also accumulated and analyzed the data published in the literature, which provided prerequisites to the generalization of the achievements in this field.

Synthesis of functionalized trichlorocyclopentenones from 1,2,3,4-tetrachloro-5,5-dimethoxypentadiene

The first representative of chlorinated cyclopentenones, *viz.*, 5-allyl derivative **2**, was prepared by the reaction of 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (**1**) with sodium allylate in DMSO.[16] The conversion **1** → **2** can be considered as a tandem process, which involves the initial nucleophilic substitution of the allylate anion for the Cl atom at the C(2) atom in diene **1** followed by the 3,3-sigmatropic rearrangement of intermediate allyl vinyl ether **3** generated *in situ* (Scheme 1).

Scheme 1



The synthetic potential of this reaction can be demonstrated with the following examples. Anions of different allylic, dienic, and eninic alcohols smoothly reacted with diene **1** to give cyclopentenones **4—12**[12,17—19] (Scheme 2).

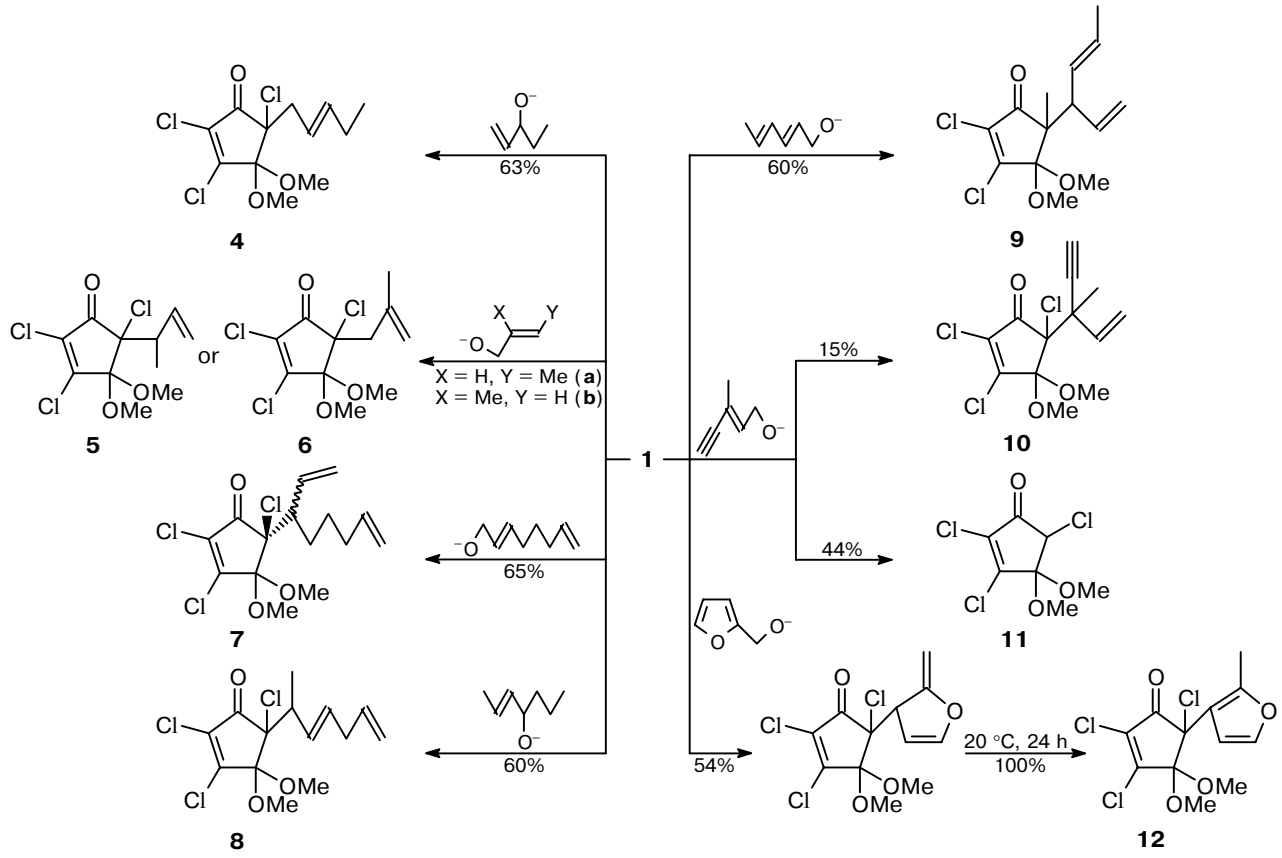
Monosodium alkoxides of *Z*- and *E*-butenediols reacted with diene **1** to yield stereoisomeric bicyclic compounds **13** and **14**, respectively.[20] Acid hydrolysis of individual compound **13** afforded a mixture of epimers of cyclopentenone **15**. The reaction of diene **1** with disodium alkoxide of *Z*-butenediol gave rise to spiromethoxy ketal **16** with an anomalous structure (Scheme 3).

An analogous reaction of a monosodium derivative of butynediol with diene **1** afforded bicyclic compound **17** containing an allenic fragment.[19] The reaction involving the propynolate anion yielded propynyl vinyl ether **18**,[21] which underwent quantitative isomerization upon vacuum distillation to form allene **19**. The possibility of the involvement of benzyl-type substrates in this reaction was exemplified[22] by the syntheses of compounds **20a—c**. The assumed mechanism of the formation of cyclopentenones **20a—c** involves the 1,3-migration of the benzylic group in intermediate **21** (Scheme 4).

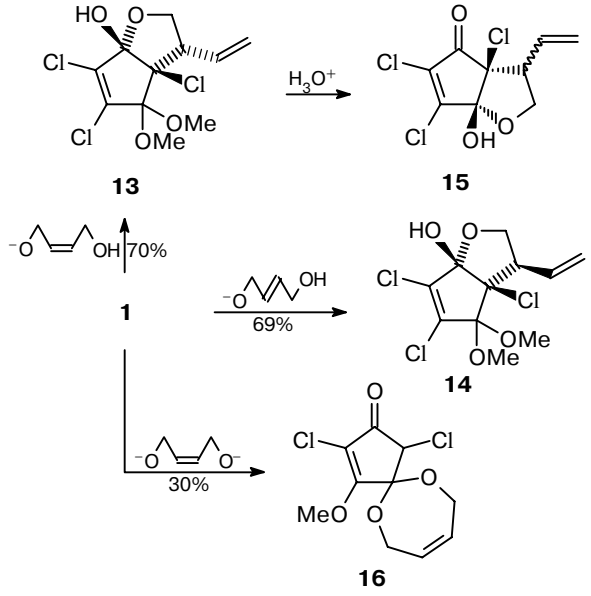
The reactions of diene **1** with a number of tertiary alkoxides always afforded trichlorocyclopentenone **11**.[12,23] This result of the reactions is accounted for by the 1,5-shift of the H atom in intermediate complex **22** (Scheme 5).

An analogous tandem process is also typical of sterically hindered secondary alcohols. In particular, the reaction of a sodium derivative of isoborneol (**23**) with diene **1** also gave rise to cyclopentenone **11**.[24] The assumed mechanism of spontaneous decomposition of ether **24** involves the intramolecular 1,6-sigmatropic proton transfer from the methyl group at the C(2) atom

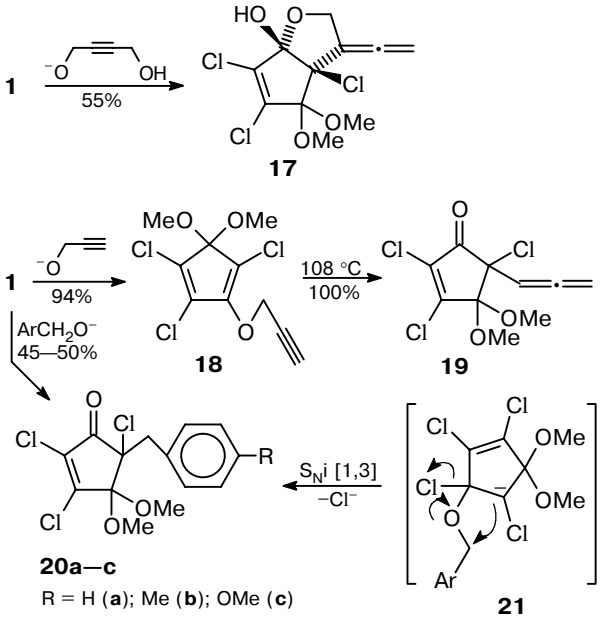
Scheme 2



Scheme 3



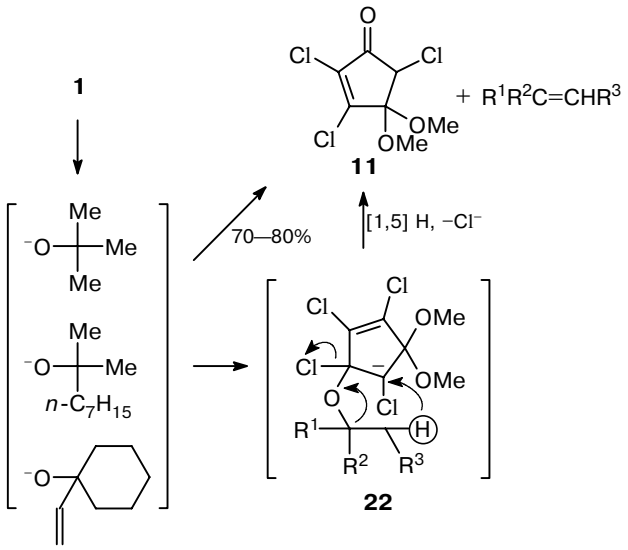
Scheme 4



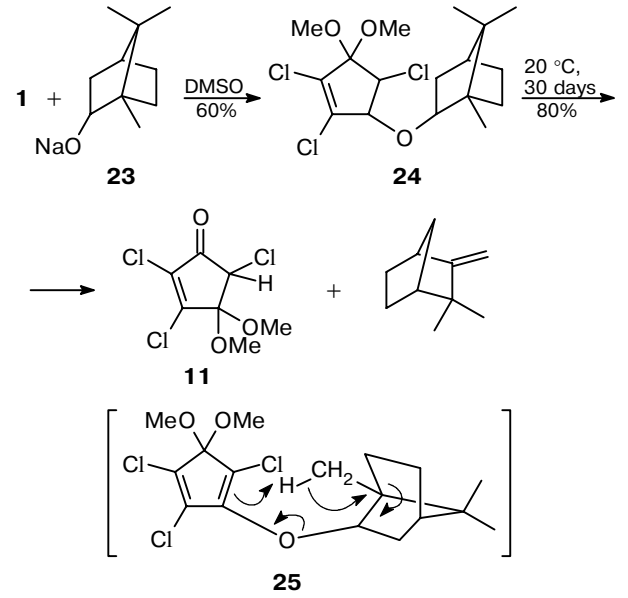
of the isobornyl fragment to the diene part of the molecule and the rearrangement of the bonds in transition state **25** (Scheme 6).

It should be noted that the synthetic equivalent of trichlorodimethoxycyclopentenone **11**, *viz.*, ethylene ketal **26**, can also be readily prepared[20] by selective hydrolysis

Scheme 5

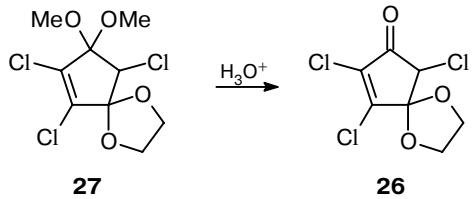


Scheme 6



of bis-ketal **27**[25] generated from compound **1** and ethylene glycol in the presence of KOH (Scheme 7).

Scheme 7



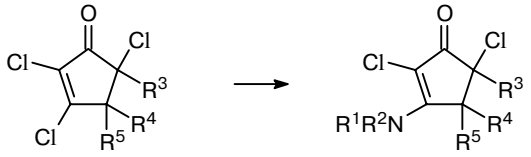
Hence, the one-pot Ad_NE—sigmatropic rearrangement tandem process involving compound **1** and alcohols made it possible to smoothly transform HCCPD into a new series of completely functionalized cyclopentenones, which are able to undergo various conversions.

Chemical properties of trichlorocyclopentenones

The structures of the above-mentioned 5-substituted trichlorocyclopentenones, which are characterized by the maximum saturation with reactive functional groups and substituents in a rather small cyclopentenone core, are of interest primarily because of their "chemical behavior" due to the possible manifestation of various assisting and cooperative effects. Hence, it seemed to be worthwhile to examine chemical properties of these compounds from the standpoint of their possible applicability in the subsequent construction of low-molecular-weight biological regulators.

Reactions of trichlorocyclopentenones with heteronucleophiles

The reactions of trichlorocyclopentenones **2**, **19**, and **26** with various nitrogen-containing nucleophiles were studied in the MeOH—KOH system.[26—28] The reactions proceeded by the Ad_NE mechanism to give the corresponding 3-*N*-substituted dichlorocyclopentenones (Table 1).



Compound	**2, 28a**	**19, 28b**	**26, 28c**
R^3	CH_2—CH=CH_2	CH=C=CH_2	H

The stages of the generation of enaminocyclopentanones **28a** from compound **2**[26] are exemplified in Scheme 8.

Scheme 8

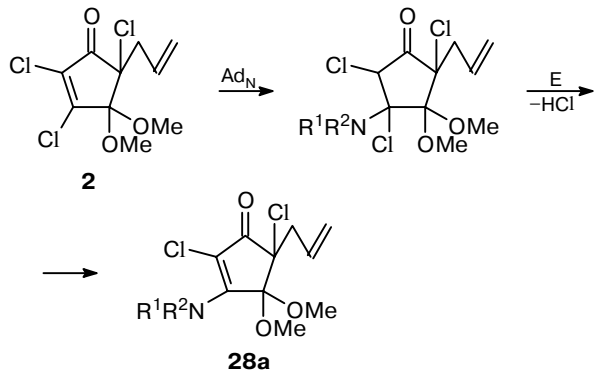
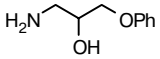
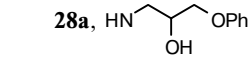
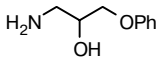
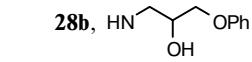
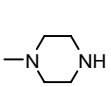
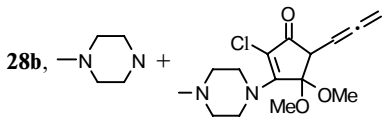


Table 1. Reactions of trichlorocyclopentenones **2**, **19**, and **26** with amines

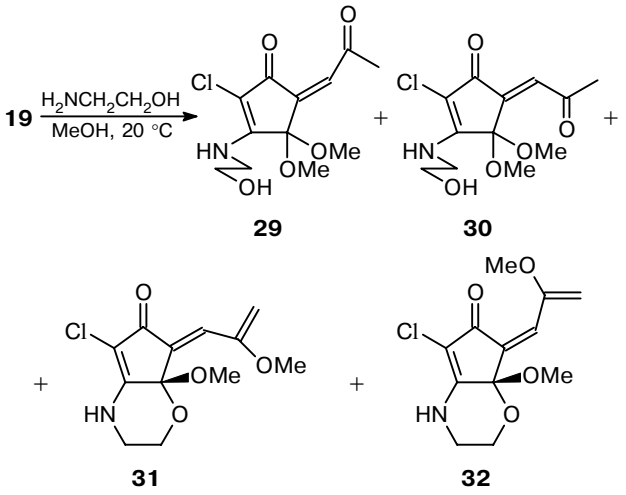
Trichloro-cyclo-pentenone	Amine	Reaction products, R^1R^2N	Yield (%)	Reference
2	$HNMe_2$	**28a**, Me_2N	90	26
	$HNEt_2$	**28a**, Et_2N	88	26
	$MeNH_2$	**28a**, MeHN	90	26
	$BuNH_2$	**28a**, BuHN	85	33
		**28a**, 	83	27
	$HOCH_2CH_2NH_2$	**28a**, $HOCH_2CH_2NH$	85	27
		**28a**, 	70	27
	$BnNH_2$	**28a**, BnHN	85	12
		**28a**,  + **28a**, 	82	27
	NH_3	**28a**, NH_2	65	29
		**28a**, 	70	12
		**28a**, 	74	27
19	$MeNH_2$	**28b**, MeHN	90	28
	$HNEt_2$	**28b**, Et_2N	90	63
		**28b**, 	85	28
		**28b**, 	88	28
		**28b**, 	81	28
		**28b**,  + **28b**, 	85	12
		**28b**, 	90	12
		**28b**, 	90	30
26		**28c**, 	90	34
	$HNMe_2$	**28c**, Me_2N	80	36
	$HNEt_2$	**28c**, Et_2N	85	34

The reaction of 2,3,5-trichloro-4,4-dimethoxy-5-propadienylcyclopent-2-en-1-one (**19**) with 2-aminoethanol in MeOH proceeded as *N*-ketovinylation with the simultaneous transformation of the side allenic substituent to form compounds **29—32** (Scheme 9).[30]

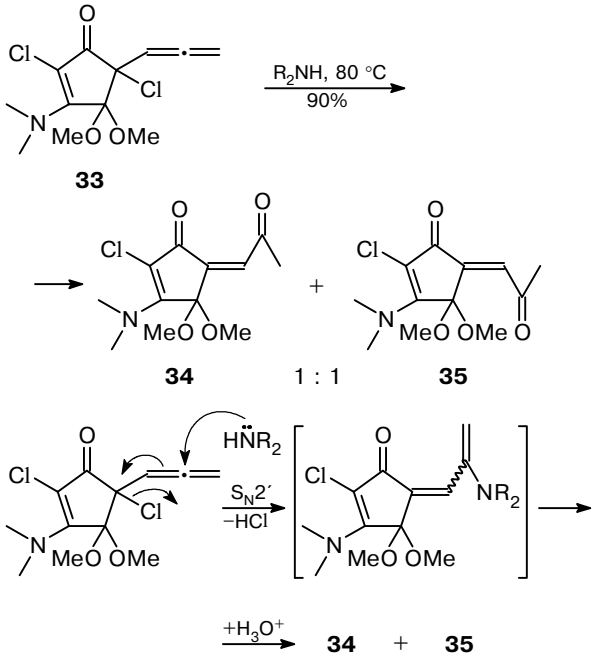
Such "oxidation" of the allenic fragment and the assumed mechanism are shown below using the reaction of compound **33** with secondary amines as an example[31] (Scheme 10).

The reactions of compound **2** with *N*-nucleophiles in the presence of a threefold excess of pyridine proceeded differently.[27] In the latter case, compounds **28a** and **36** were obtained in a ratio of 1 : 1 (Scheme 11).

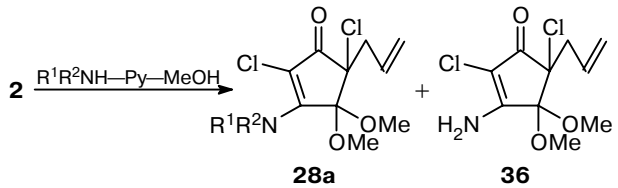
Scheme 9



Scheme 10

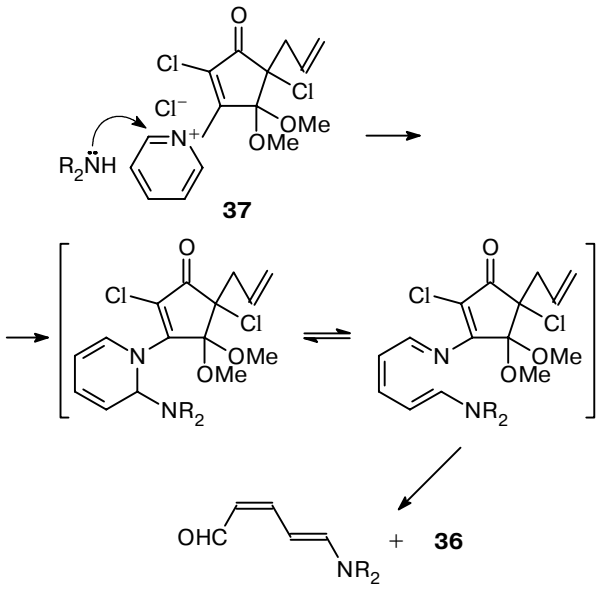


Scheme 11



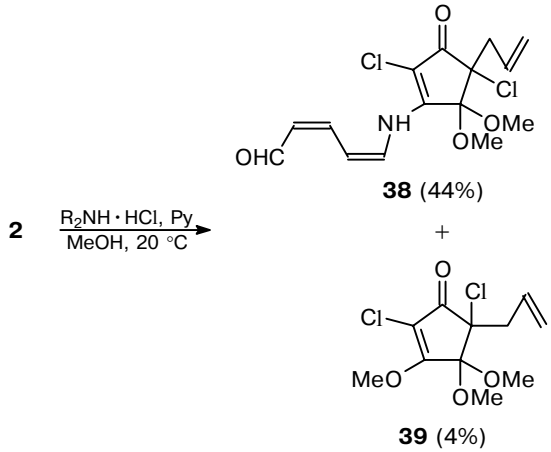
In the absence of amine in a methanol medium, pyridine readily reacted with chlorovinyl ketone **2** to yield water-soluble brown ionic complex **37**. Based on this fact, it was suggested[27] that the reaction in the presence of amine proceeded through complex **37**, which then reacted with the amine resulting in the pyridine-ring opening to give enaminochloroketone **36** (Scheme 12).

Scheme 12



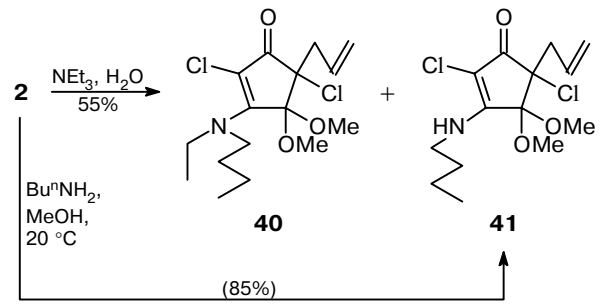
The reactions with the use of hydrochlorides of sterically hindered dicyclohexyl- and diisopropylamines[27,32] afforded *N*-dienal **38** as well as methoxy derivative **39** as the minor product (Scheme 13).

Scheme 13



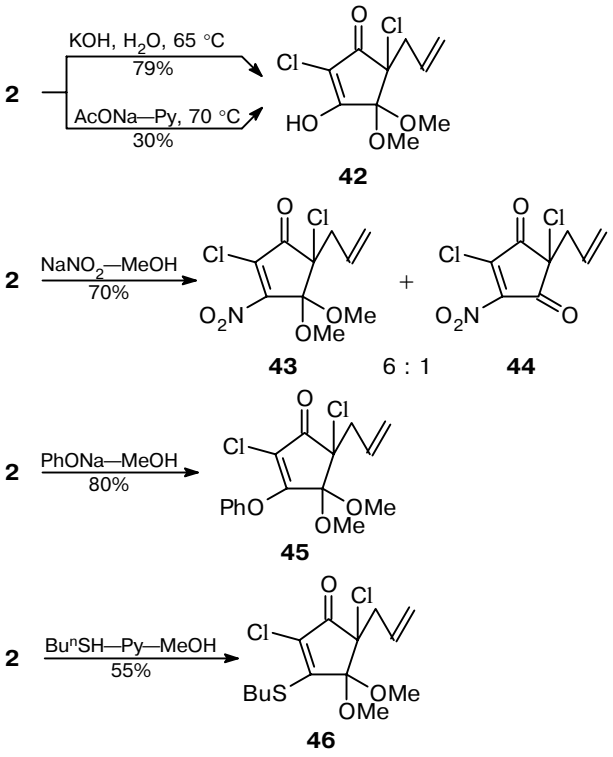
An interesting conversion of ketone **2** was observed in boiling triethylamine containing 1—2 equiv. of water. This reaction gave rise to enaminoketones **40** and **41** (2 : 3) in a total yield of 55%. Compound **41** was also prepared[33] by the direct reaction of ketone **2** with Bu^nNH_2 (Scheme 14).

Scheme 14



The reactions of compound **2** with the acetate, hydroxy, nitrite, and phenoxide anions and with butanethiol were investigated.[27] Unlike amines, the above-mentioned nucleophiles are less reactive in β-ketovinylation (Scheme 15).

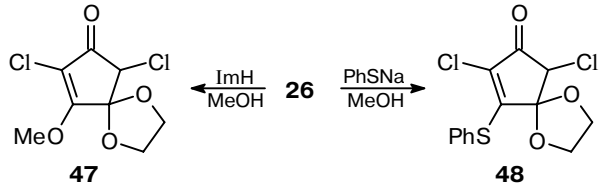
Scheme 15



O-Ketovinylation product **47** was prepared by the reaction of enone **26** in the MeOH—imidazole medium.[34] *S*-Ketovinylation product **48** was obtained in 55% yield by the reaction of ethylene ketal **26** with PhSNa (Scheme 16).

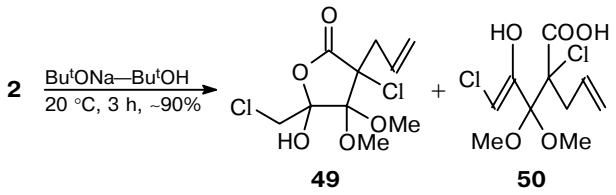
Although the above-discussed β-ketovinylation reactions of nucleophiles involving trichloroketones **26** and ketone **2** proceeded primarily as the replacement of the vinylic Cl atom at C(3), it was demonstrated[35] that the reaction of compound **2** with Bu^{t}ONa in Bu^{t}OH took

Scheme 16



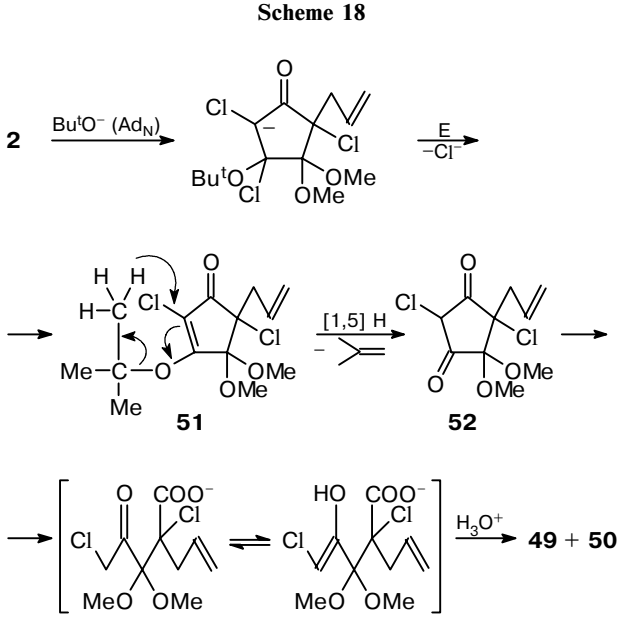
an unusual path to give lactone **49** and acid **50** in high yield in a ratio of 1 : 1.4 (Scheme 17).

Scheme 17



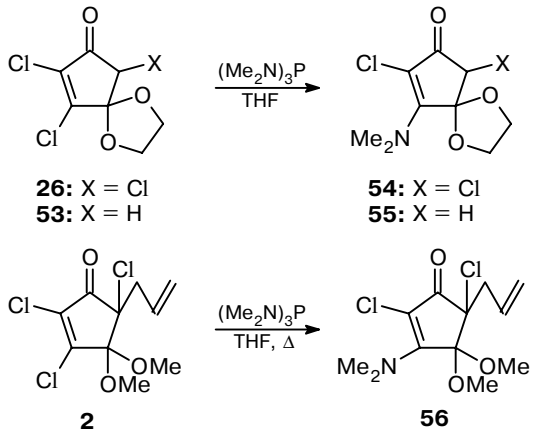
The probable mechanism of this conversion involves the retroene-type fragmentation of primary substitution adduct **51** and the retro-Claisen cleavage of intermediate 1,3-diketone **52** (Scheme 18).

Scheme 18



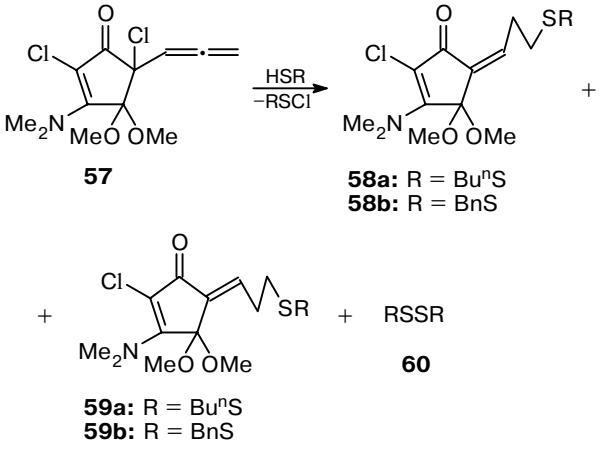
The reactions of tri- and dichlorocyclopentenones (**2** and **53**, respectively) with an equimolar amount of $P(NMe_2)_3$ in boiling THF afforded[36] compounds **55** and **56**, respectively, in ~80% yields. An analogous reaction of trichlorocyclopentenone **26** proceeded under milder conditions (THF, 20 °C) to form 2,5-dichloro-3-dimethylamino-4,4-ethylenedioxycyclopent-2-en-1-one **54** in 85% yield (Scheme 19).

Scheme 19



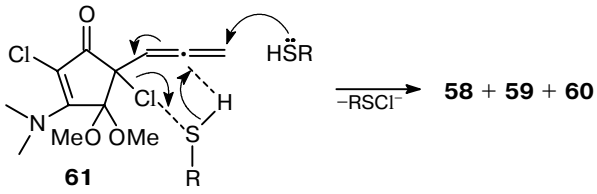
Nucleophilic thiylation of 2,5-dichloro-3-dimethylamino-4,4-dimethoxy-5-propadienylcyclopent-2-en-1-one (**57**) with butane- and toluenethiols proceeded unusually[37] to give addition products at the terminal atom of allene **57**, *viz.*, **58a,b** and **59a,b**, respectively, and symmetrical disulfides **60** in good yields. Isomeric exocyclic α,β-unsaturated ketones *Z*-**58** and *E*-**59** were obtained in a ratio of ~1 : 2 (Scheme 20).

Scheme 20



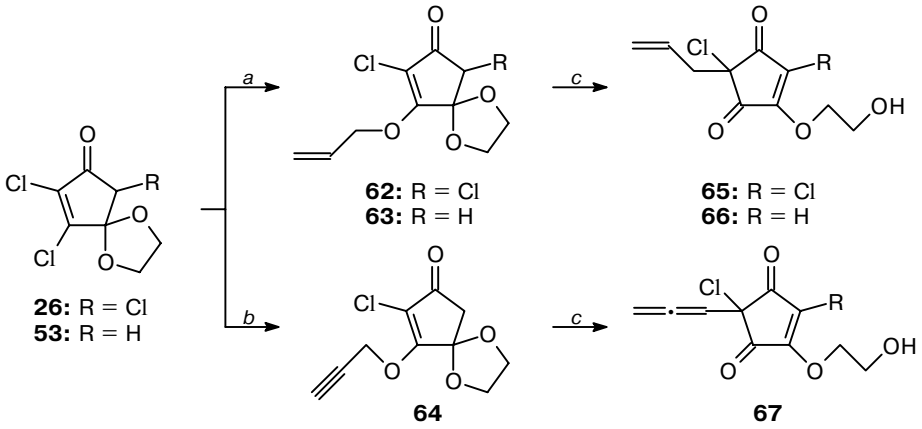
The reaction proceeded, apparently, through intermediate six-membered transition complex **61** and involved elimination of the Cl^- ion (as RSCl) followed by the migration of the internal double bond in the allene fragment with the synchronous transfer of the hydride ion and the addition of HSR to the terminal atom of the allene group (Scheme 21).

Scheme 21



The tendency of compounds **26** and **53** to enter into reactions with various N-, O-, and S-nucleophiles resulting in the replacement of the vinyl Cl atom at the C(3) atom allowed the synthesis[38] of the corresponding vinyl ethers of allyl and propargyl alcohols **62—64**. The latter compounds were tested under the conditions of the thermal Claisen rearrangement. The above-mentioned rearrangements of ethers **62—64** proceeded upon refluxing in toluene with the simultaneous dioxolane-ring opening and β-elimination to produce compounds **65—67**, respectively, in good yields (Scheme 22).

Scheme 22

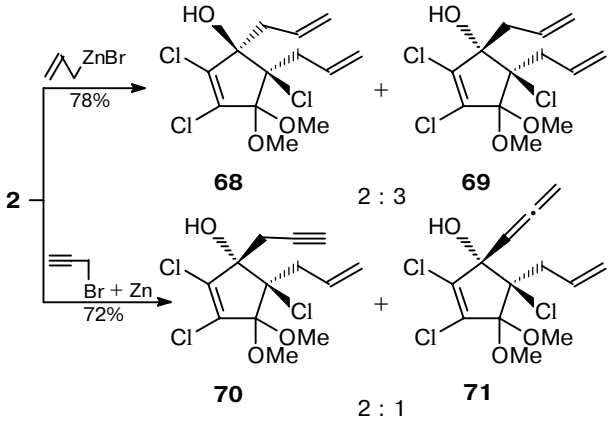


Reagents and conditions: *a*. CH_2=$CHCH_2ONa$, THF, 20 °C; *b*. HC≡CCH_2ONa, THF, 20 °C; *c*. PhMe, Δ.

Reactions of di- and trichlorocyclopentenones and their derivatives with some CH acids and organometallic compounds

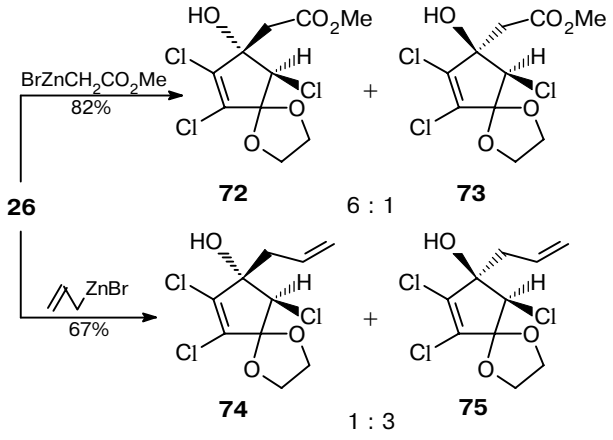
The reactions of trichlorocyclopentenone **2** with Reformatsky reagents, which were generated *in situ* from methyl(ethyl) bromoacetates or allyl(propargyl) bromides and Zn in DMF, resulted in the chemoselective 1,2-addition of nucleophiles to the carbonyl group of **2**[39] (Scheme 23).

Scheme 23



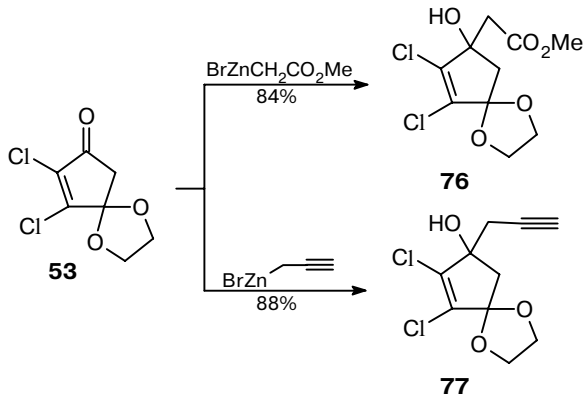
Analogous reactions of $BrZnCH_2CO_2Me$ and $CH_2{=}CHCH_2ZnBr$ with compound **26** also proceeded chemoselectively to form the corresponding isomeric chlorohydrins (Scheme 24).

Scheme 24



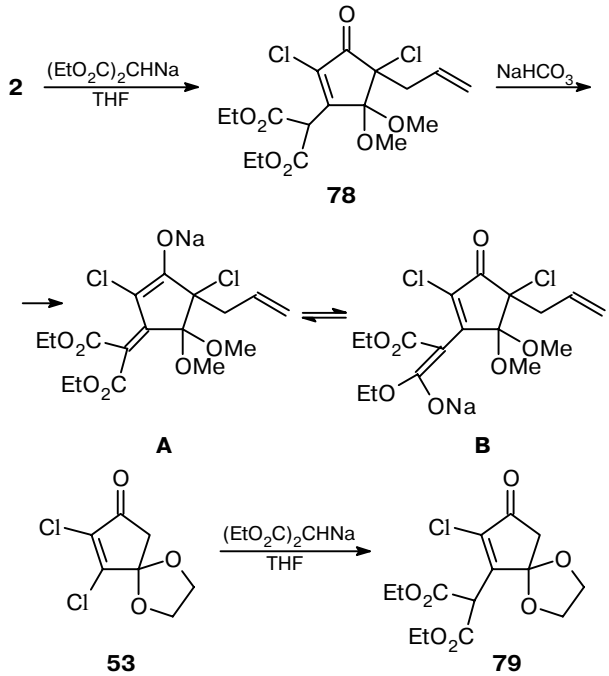
Condensation of dichlorocyclopentenone **53** with $BrZnCH_2CO_2Me$ and $CH{\equiv}CCH_2ZnBr$ afforded the expected tertiary alcohols **76** and **77**, respectively, in good yields (Scheme 25).

Scheme 25



Chlorocyclopentenones **2** and **53** reacted with sodium diethyl malonate to give products of the Ad_NE-substitution of the vinylic Cl atom at C(3), *viz.*, compounds **78** and **79**, respectively, in ~90% yields.[40] It was noted that the related stabilized carbanions of acetoacetic and cyanoacetic esters did not react with the above-mentioned enones. Compounds **78** and **79** were readily dissolved in aqueous solutions of $NaHCO_3$ to give bright-red solutions of enolates **A** and **B** (Scheme 26).

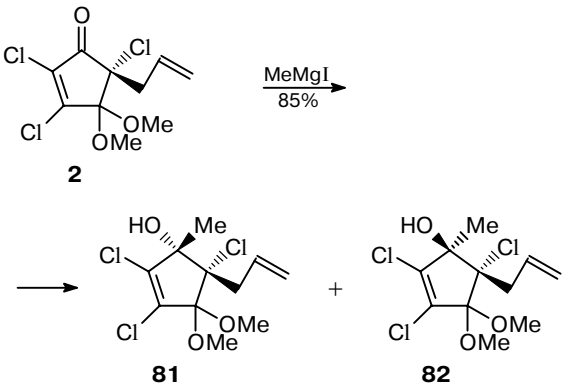
Scheme 26



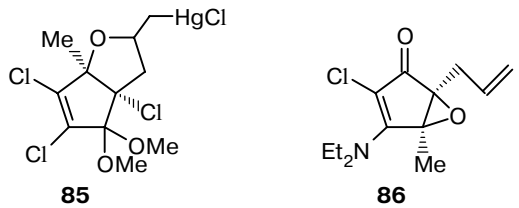
Interesting inversions of the diastereofacial selectivity were observed in the reactions of MeMgI with related cyclopentenones **2** and **80**.[41,42] Enone **2** reacted with 1.5 equiv. of MeMgI to give a mixture of epimeric alcohols **81** and **82** in a ratio of 4 : 1 in a total yield of 85%. The stereochemical result is indicative of the steric

control over the reaction. Thus, the bulky Cl atom at C(5) directs the attack of the reagent from the β region of molecule **2**. However, another direction and the opposite selectivity were observed in an analogous reaction of enaminodiketone **80** with MeMgI producing epimeric alcohols **83** and **84** in a ratio of 9 : 1 in a total yield of 93% (Scheme 27).

Scheme 27

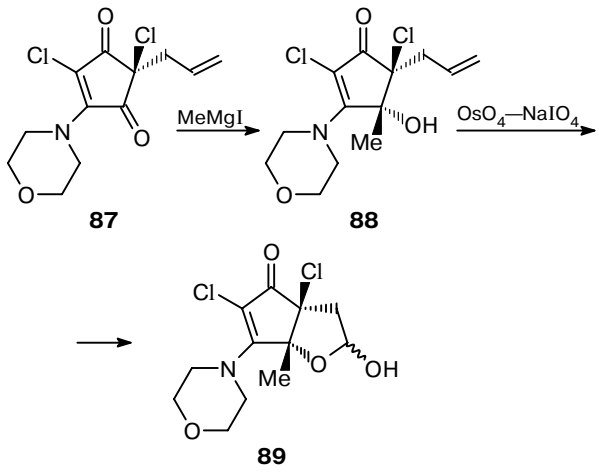


The structures of these reaction products were also confirmed by the conversions of epimer **82** into bicyclic compound **85** and of epimer **83** into epoxide **86**.



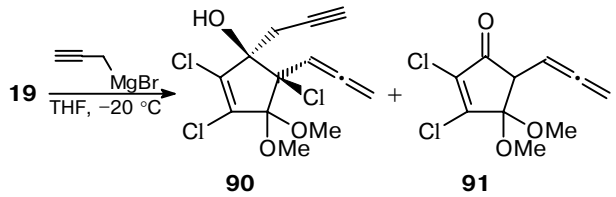
Condensation of diketone **87** with MeMgI, like that of **80**, gave rise to *trans*-chlorohydrin **88**. The stereochemistry of the substituents was confirmed[43] by the conversion of **88** into lactol **89** (Scheme 28).

Scheme 28



The reaction of compound **19** with propargylmagnesium bromide in THF at 20 °C afforded *cis*-chlorohydrin **90** and allenyl ketone **91** in approximately equal yields[30] (Scheme 29).

Scheme 29

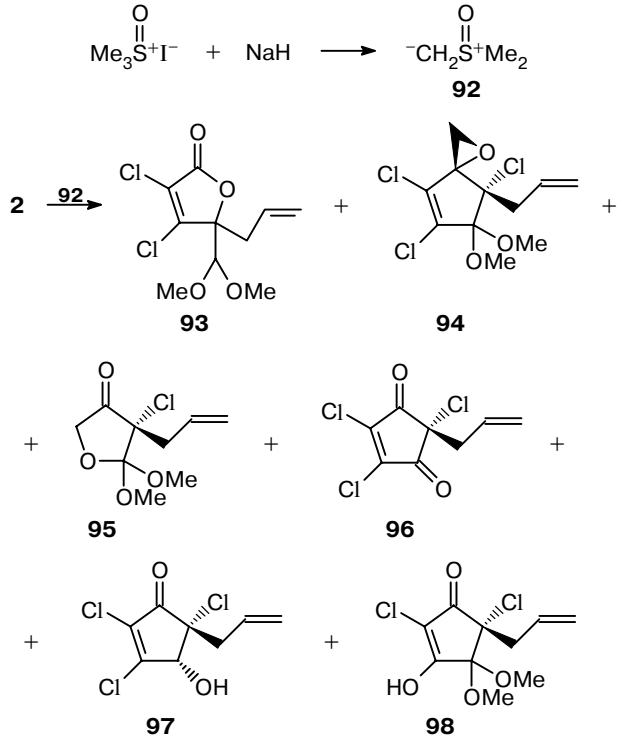


In the reaction with ylide **92**, cyclopentenone **2** behaved as a chemical chameleon to give compounds **93—98** in various ratios depending on the reaction conditions. The mechanisms of formation of compounds **93** and **95** with anomalous structures accompanied by the deep reorganization of the skeleton of **2** and changes of the degrees of oxidation of particular carbon atoms are not entirely known[44] (Scheme 30).

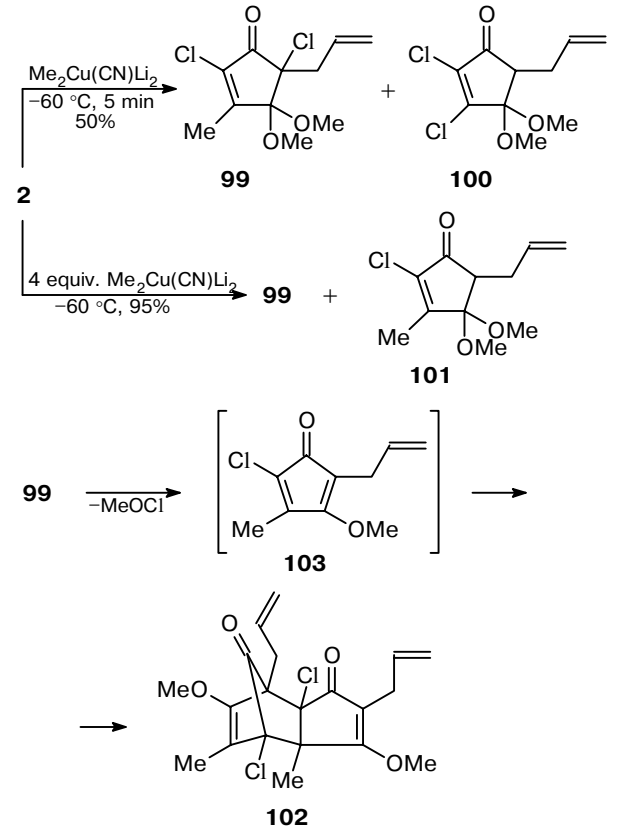
The behavior of trichlorocyclopentenones under the reaction conditions involving cuprates is of interest. Thus, the reaction of enone **2** with 2.5 equiv. of $Me_2Cu(CN)Li_2$ afforded compounds **99** and **100** in a ratio of 7 : 1 in 50% yield.[34] An increase of the amount of the cuprate reagent used in the reaction to 4 equivalents made it possible to increase the total yield of compounds **99** and **101** (6 : 4) to 95%. It was mentioned that storage of purified specimens of **99** resulted in the slow uncatalyzed formation of diketone **102**. Compound **102** was, apparently, derived from highly reactive cyclopentadienone **103**, which was generated from **99** by homolytic elimination of MeOCl (Scheme 31).

Depending on the conditions, an analogous reaction of enone **26** with $Me_2Cu(CN)Li_2$ can give rise to acyclic acids **105** and **106** as by-products[34,45] (Scheme 32).

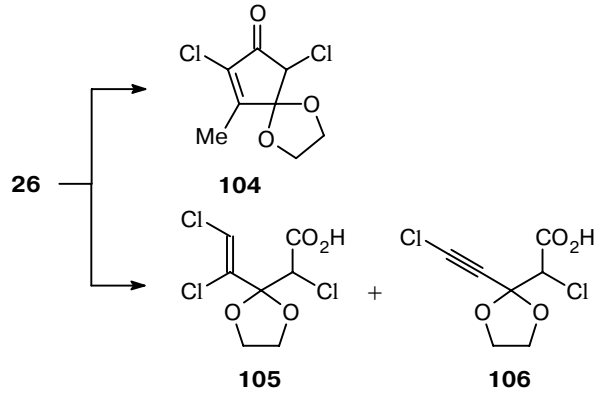
Scheme 30



Scheme 31



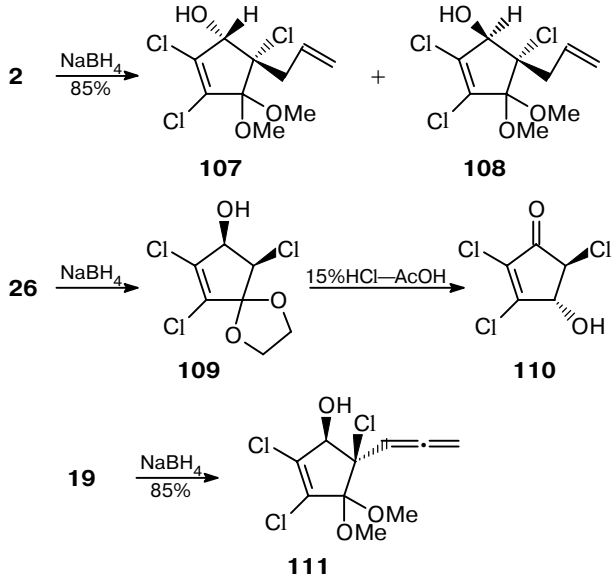
Scheme 32



Reactions of chlorocyclopentenones with reducing agents

Sodium borohydride is quite suitable for chemoselective reduction of the keto group in trichlorocyclopentenones. Ketone **2** was reduced by $NaBH_4$ with high stereoselectivity to give *cis*- (**107**) and *trans*-chlorohydrins (**108**) in a ratio of 95 : 5.[41,46] The reaction of chloroketone **26** afforded[47] exclusively *cis*-chlorohydrin **109**. Borohydride reduction of allenyl ketone **19** was also highly stereoselective and produced *cis*-chlorohydrin **111** in quantitative yield. The observed stereochemical result of the reaction is governed by the virtually total steric control over the direction of the attack of the reagent by the Cl atom at C(5) (Scheme 33).

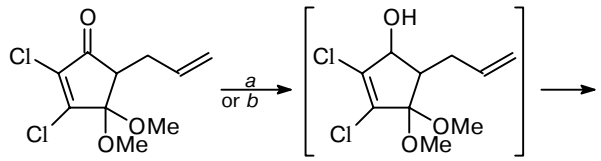
Scheme 33

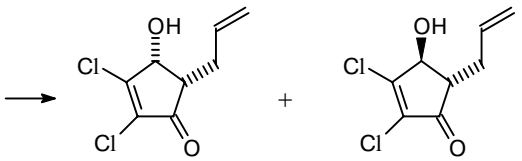


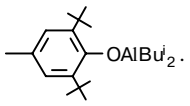
The use of more stereodifferentiating reducing agents (L-selectride, DIBAH, *etc.*) allows one to prepare exclusively *cis*-chlorohydrins starting from trichlorocyclopentenones.

A different situation was observed in the case of reduction of dichloro derivative **100**. Reduction of the latter under the action of $NaBH_4$ in 96% ethanol afforded[46] directly keto alcohols **113** and **114** in a ratio of 45 : 55. The reaction involving the bulky Yamamoto reducing reagent (the conditions *b*) gave rise to compounds **113** and **114** in a ratio of 75 : 25. Apparently, spontaneous deketalization of intermediate **112** occurred due to the intramolecular effect of the free hydroxy group (Scheme 34).

Scheme 34

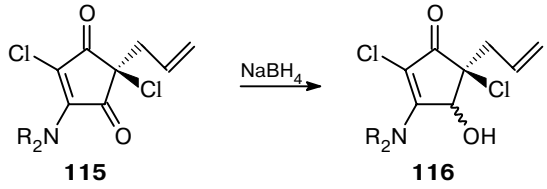




Reagents and conditions: *a*. $NaBH_4$; *b*. 

Unlike the above-considered di- and trichlorocyclopentenones, the keto group of the vinylogic amide in diketones **115** is inert with respect to standard reducing reagents[12] (Scheme 35).

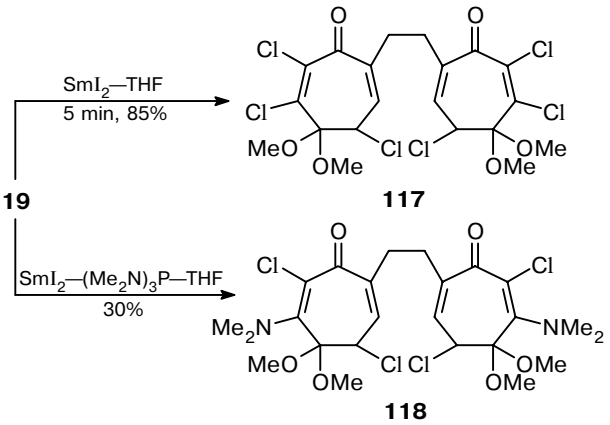
Scheme 35



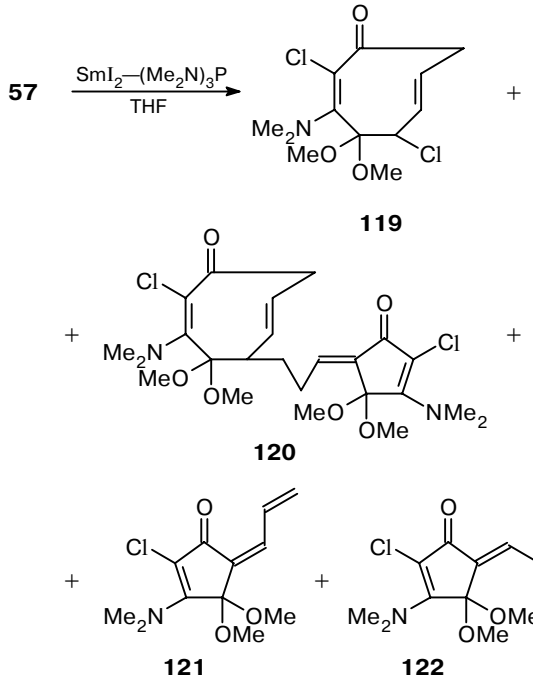
Under the action of the one-electron reducing agent SmI_2—THF, allenyl ketone **19** was rapidly converted into bis-troponoethane derivative **117**.[48] Analogously, compound **19** was converted into **118** in the SmI_2—HMPT—THF system (Scheme 36).

The reaction of dimethylamino derivative **57** with SmI_2 in THF containing $(Me_2N)_3P$ proceeded somewhat differently.[49] Thus, amine **57** was rapidly converted into a mixture of compounds **119—122**. The total yield of compounds **119—122** was higher than 80%; the ratio **119** : **120** : **121** : **122** = 38 : 33 : 10 : 19 (Scheme 37).

Scheme 36



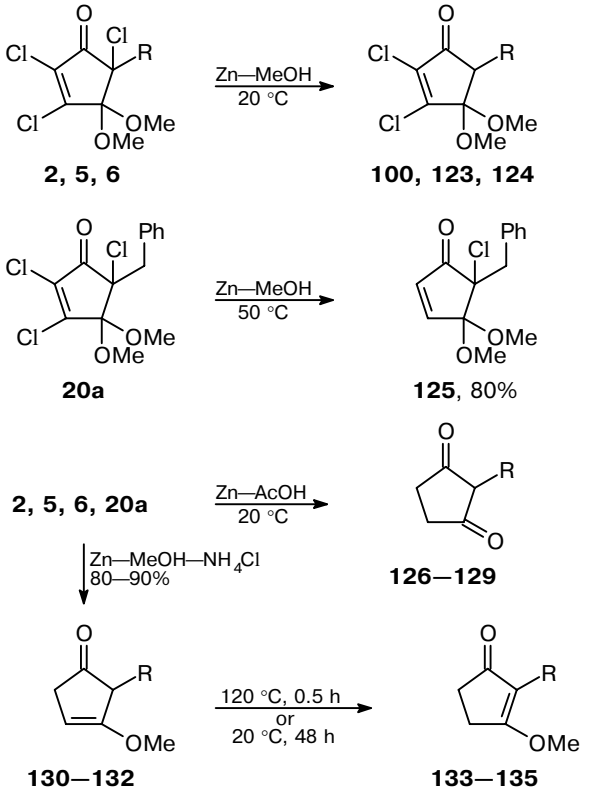
Scheme 37



Partial and exhaustive reductive dechlorination of substrates **2**, **5**, **6**, and **20a** were investigated with the use of the Zn—MeOH, Zn—AcOH, and Zn—MeOH—NH_4Cl systems.[50] Depending on the reaction conditions, dichloro derivatives **100**, **123**, and **124**, exhaustive dechlorination products **130—132**, or cyclopentanediones **126—129** were obtained in high yields; isomeric enol ethers **133—135** were also isolated. The spectral data (^1H and ^{13}C NMR and IR) and the results of X-ray diffraction analysis unambiguously indicated that diketones **126—129** existed exclusively as enols both in solutions and in the crystalline state[51] (Scheme 38).

Compound **26** was subjected to selective monodechlorination under the action of $CrCl_2$ to obtain **53**.[52]

Scheme 38



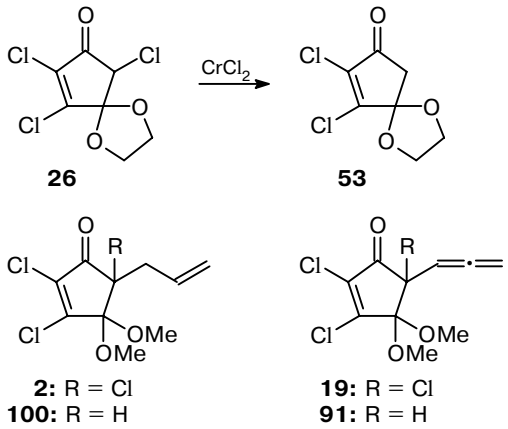
Compound	R	Yield (%)
100		80
126		90
130		~100
123		75
127		78
131		~100
124		66
128		90
132		~100
129	Bn	~87

Under the action of this reagent, compounds **2** and **19** were regioselectively reduced to produce compounds **100** and **91** in 82 and 71% yields, respectively (Scheme 39).

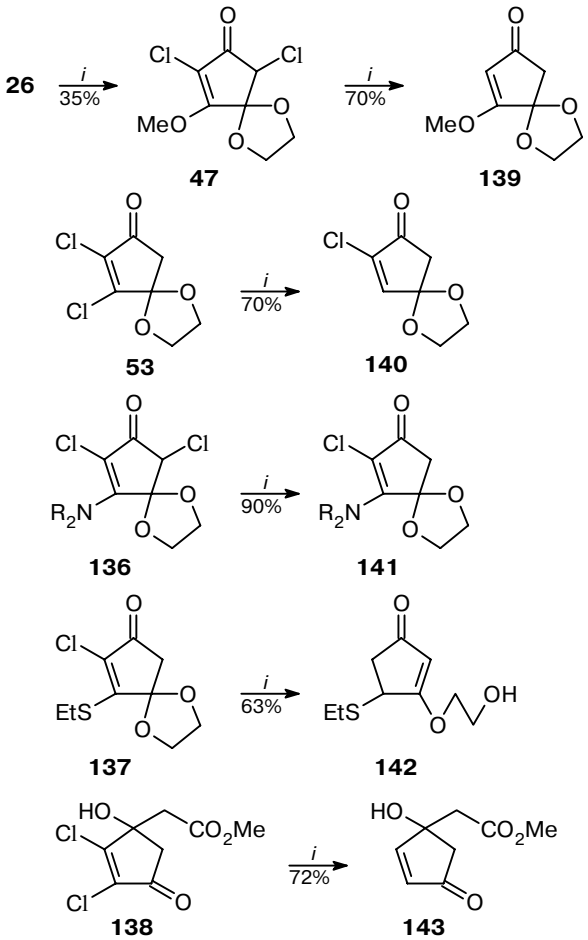
The behavior of trichlorocyclopentenone **26** and related compounds **47**, **53**, and **136—138** was examined under the action of the mild reducing system Zn—MeOH—NH_4Cl.[53] In spite of the similar chemical nature, the above-mentioned compounds entered into this reaction to give dechlorination products **139—143** of different types (Scheme 40).

Because of the asbence of the activating carbonyl group, compound **27**, unlike the above-mentioned chlorocyclopentenones, can be subjected to reductive dechlorination only with the use of the strongest reagent, *viz.*, $LiAlH_4$[47] (Scheme 41).

Scheme 39



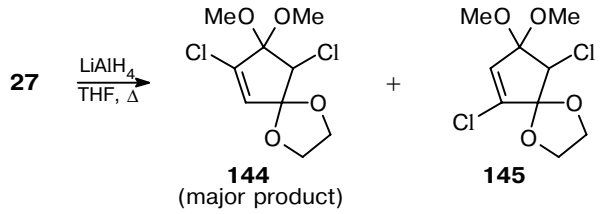
Scheme 40



Reagents and conditions: *i*. Zn, NH_4Cl, MeOH.

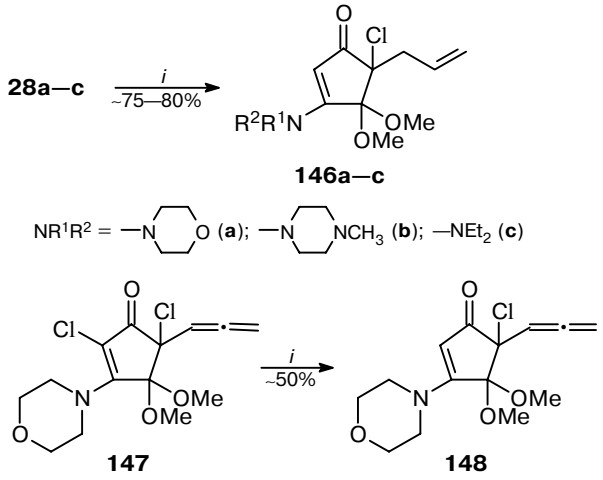
It was demonstrated[54] that enaminochloroketones of cyclopentane series **28a—c** reacted with Me_3SiI to give C(2)-dechlorinated cyclopentenones **146a—c** in good yields. Under analogous conditions, 5-allenylcyclo-

Scheme 41



pentenone **147** also generated reductive dechlorination product **148** (Scheme 42).

Scheme 42



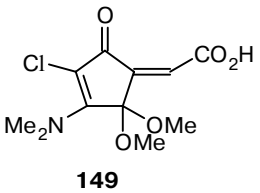
Reagents and conditions: *i.* 4 equiv. of Me_3SiI, MeCN, 20 °C, 1 h.

Reactions of trichlorocyclopentenones and their derivatives with oxidizing agents

Reactions of trichlorocyclopentenones and their derivatives with oxidizing agents are of particular interest. The presence of several potentially reactive centers and a system of double bonds characterized by different degrees of activation and steric accessibility is responsible for the unusual chemical behavior of sterically crowded polyheterofunctionalized cyclopentenones in reactions with oxidizing agents as exemplified by the reactions presented in Table 2.

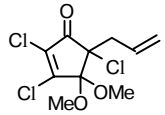
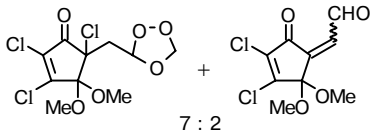
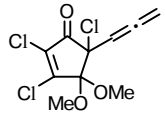
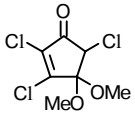
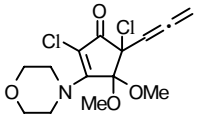
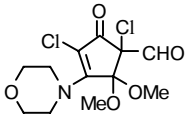
The possibilities of selective oxidation of the side double bonds in the above-mentioned cyclopentenones and the characteristic features of the behavior of 2,3-dichlorocyclopentenones and their 3-morpholine derivatives were demonstrated using the reactions of trichlorocyclopentenones with O_3 and MnO_4^- as examples (Table 2, reactions 1—6).[55—58] These characteristic features are determined by the difference in the electron density in their C(1)-carbonyl group, which exerts a substantial effect both on the reaction pathway and the stereospecificity of some transformations.

In experiments on catalyzed periodate oxidation (Table 2, reactions 7—17),[28,43,59—63] noteworthy is the exclusively stereoselective formation of 5*Z*-isomeric acids from 3-amino derivatives of 5-allenyldichlorocyclopentenones (Table 2, reaction 15). The structure of one representative (5*Z*-carboxymethylidenecyclopentenone **149**)



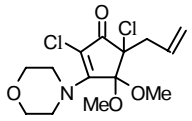
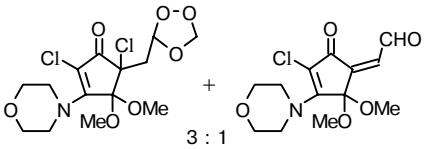
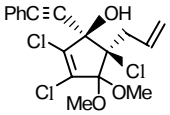
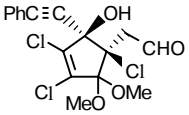
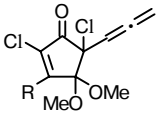
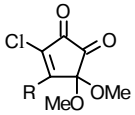
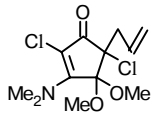
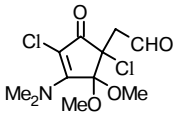
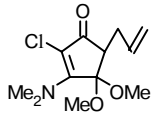
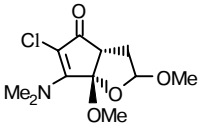
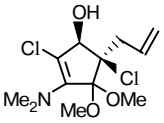
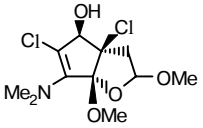
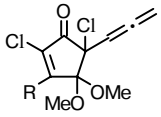
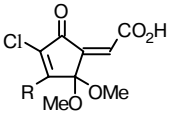
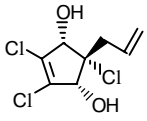
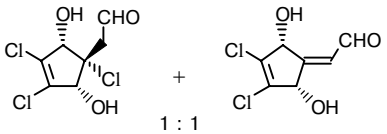
149

Table 2. Oxidation of chlorocyclopentenones, their derivatives, and analogs

Reaction	Substrate	Oxidant (conditions)	Products	Yield (%)	Reference
1		O_3 (1) CH_2Cl_2, −78 °C; 2) Me_2S)	 7 : 2	90	57
2		The same		85	57
3		»		90	56

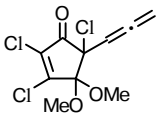
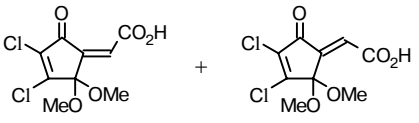
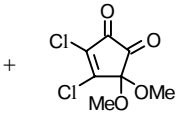
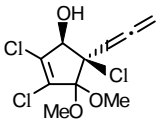
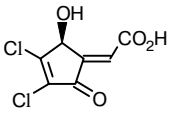
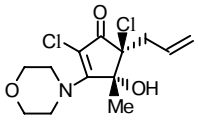
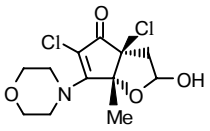
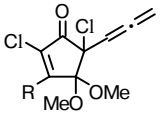
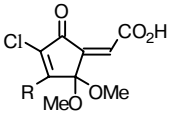
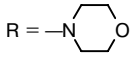
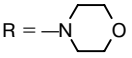
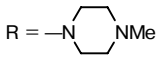
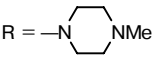
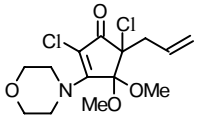
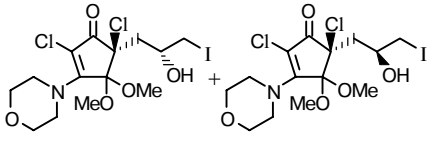
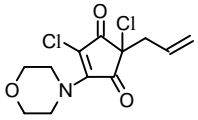
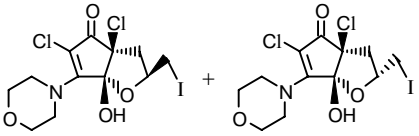
(*to be continued*)

Table 2 (*continued*)

Reaction	Substrate	Oxidant (conditions)	Products	Yield (%)	Reference
4		»	 3 : 1	80	56
5		»		60	58
6		$KMnO_4$—$Et_3N^+BnCl^-$ (CH_2Cl_2, 20 °C)			55
	R = —NEt_2		R = —NEt_2	60	
	R = —N O		R = —N O	70	
	R = Cl		R = Cl	0	
7		OsO_4 (catalyst)—$NaIO_4$		88	62
8		The same		42	62
9		»		>95	62
10		»			28
	R = —NMe_2		R = NMe_2	86	
	R = —N O		R = —N O	81	
11		OsO_4 (catalyst)—$NaIO_4$	 1 : 1	55	59

(*to be continued*)

Table 2 (*continued*)

Reaction	Substrate	Oxidant (conditions)	Products	Yield (%)	Reference
12		The same		58	62
				30	
13		»		52	62
14		»		63	43
15		$RuCl_3$ (catalyst)—$NaIO_4$ (CCl_4—MeCN—H_2O)			63
	R = —NMe_2		R = NMe_2	90	
	R = —NEt_2		R = NEt_2	88	
				95	
				93	
16		The same	 8 : 1	51	61
17		»	 10 : 1	62	61

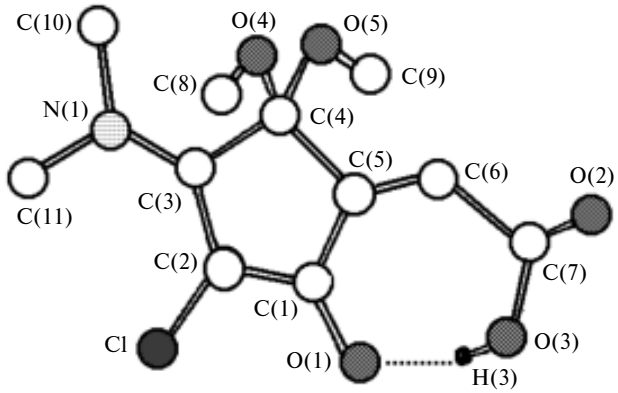


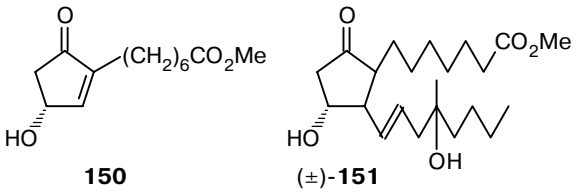
Fig. 1. Three-dimensional molecular structure of 5*Z*-carboxymethylene-2-chloro-3-dimethylamino-4,4-dimethoxycyclopent-2-en-1-one (**149**).

was also established by X-ray diffraction analysis (see Fig. 1).[60]

In addition, it should be noted that $RuCl_3$-catalyzed periodate oxidation of 3-morpholine derivatives of 5-allyldichlorocyclopentenones proceeded anomalously to yield isomeric iodohydrins (Table 2; reactions 16 and 17).[61]

Use of chlorocyclopentenones in the synthesis of biologically active cyclopentanoids

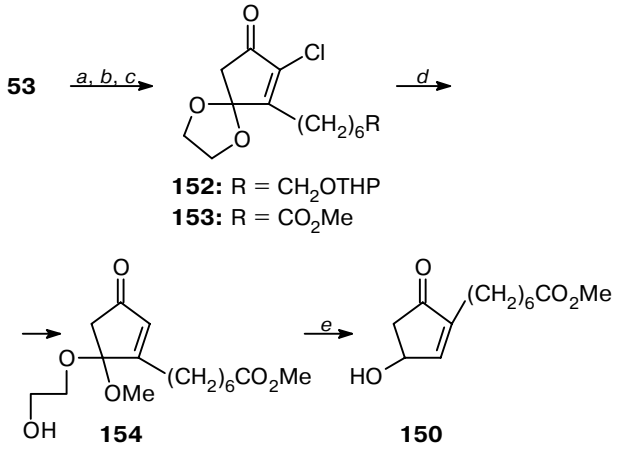
Both chiral and racemic cyclopentenones **150** are widely used in the convergent cuprate approach to prostaglandins.[64] In particular, misoprostol **151**, which is an analog of prostaglandin E_1 exhibiting the antisecretory action, was synthesized starting from (±)-**150**.[65,66]



A feasible procedure was developed for the synthesis of compound (±)-**150** from dichlorocyclopentenone **53**.[67] Initially, ether **152** was synthesized by the Ad_NE-addition of $THPO(CH_2)_7MgBr/CuI$ to compound **53**. Then compound **152** was subjected to oxidation with the Johnes reagent and methylation with CH_2N_2 to obtain ester **153**. Subsequent mild reductive dechlorination (Zn—MeOH—NH_4Cl) of compound **153**, borohydride reduction of the resulting enone **154**, and purification of the product on SiO_2 produced enone **150**. The total yield of (±)-**150** was 20—25% with respect to the starting dichlorocyclopentenone **53** (Scheme 43).

4-Hydroxycyclopent-2-en-1-one derivatives **155** are often used in the synthesis of prostanoids according to the double convergent coupling.[68—70] New 4-hydroxycyclopentenones **156—158** were synthesized from **53**.[71]

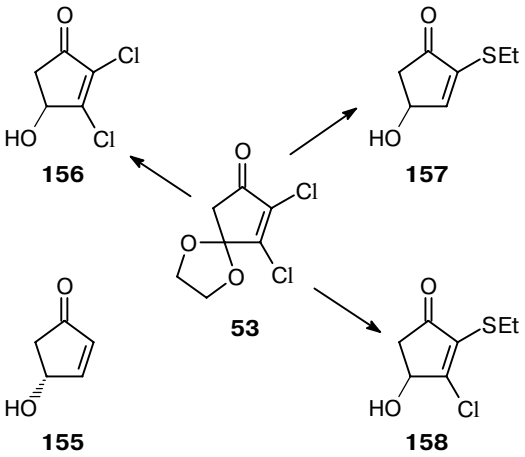
Scheme 43



Reagents and conditions: *a*. $THPO(CH_2)_7MgBr$, CuI; *b*. 5 equiv. of H_2CrO_4, 20 °C, 1 h; *c*. CH_2N_2, 0 °C; *d*. Zn, MeOH, NH_4Cl; *e*. $NaBH_4$, EtOH, 0 °C.

These compounds are of interest as potential starting reagents for the development of procedures for 2,3-vicinal dialkylation of 4-hydroxycyclopent-2-en-1-ones methodologically different from the double convergent coupling (Scheme 44).

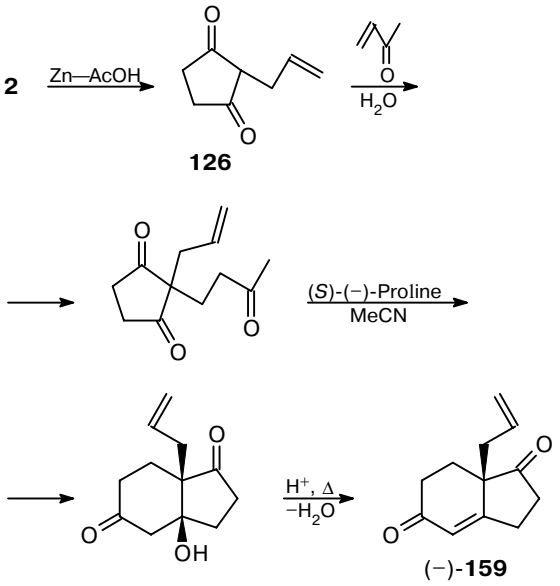
Scheme 44



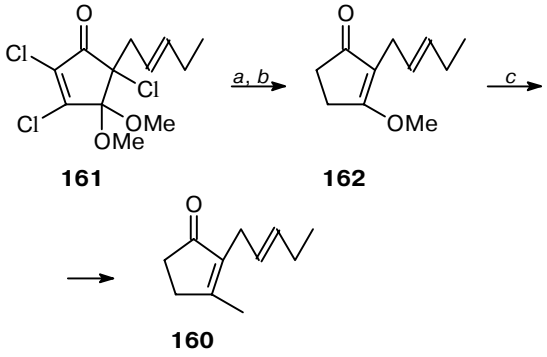
Trichlorocyclopentenone **2** was used in the synthesis of new chiral indanedione **159** containing the readily functionalized angular allyl substituent suitable for the construction of bridged polycyclic systems.[72] The synthesis of compound **159** was based on transformations of 2-allylcyclopentanedione **126** according to a scheme developed in the study[11] (Scheme 45).

A simple procedure was devised for the preparation of *E*-jasmone **160** based on **161**.[17] The synthetic scheme involves exhaustive reductive dechlorination of trichloroketone **161** to form ketoenol ether **162** followed by smooth condensation with MeMgI (Scheme 46).

Scheme 45

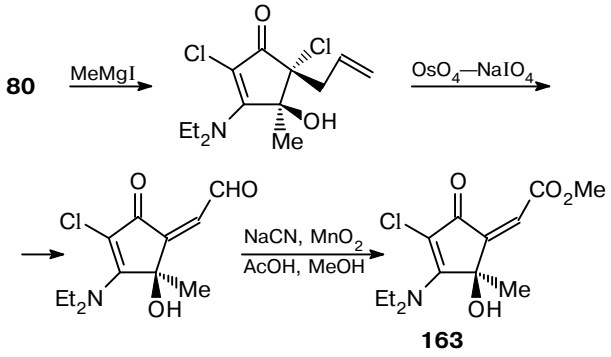


Scheme 46

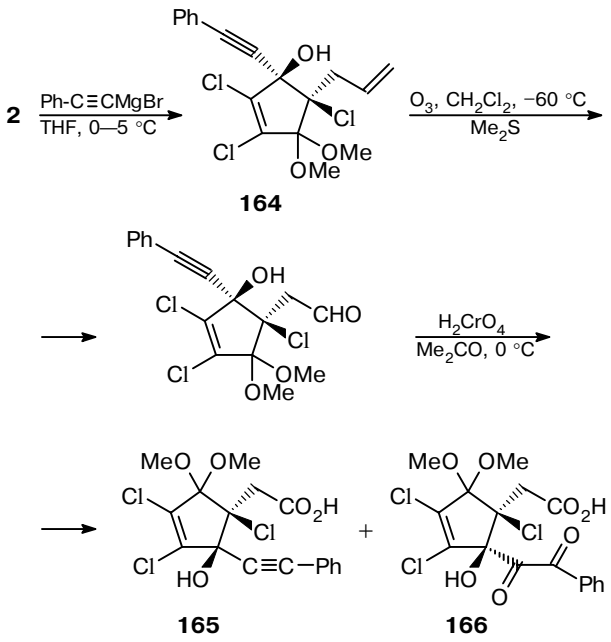


Reagents and conditions: *a.* Zn—MeOH—NH_4Cl; *b.* 120 °C, 0.5 h; *c.* MeMgI, Et_2O, −20 °C.

Scheme 47



Scheme 48



Readily accessible enaminochloroketone **80** was used in the synthesis of compound **163**, which can be considered as the simplest representative of analogs of sea prostanoids[41] (Scheme 47).

Analogously to the above-considered scheme, acetylenic alcohol **164**, which was generated from compound **2**, was transformed into pharmacologically promising cyclopentanoids **165** and **166**[58] bioisosteric to **163** (Scheme 48).

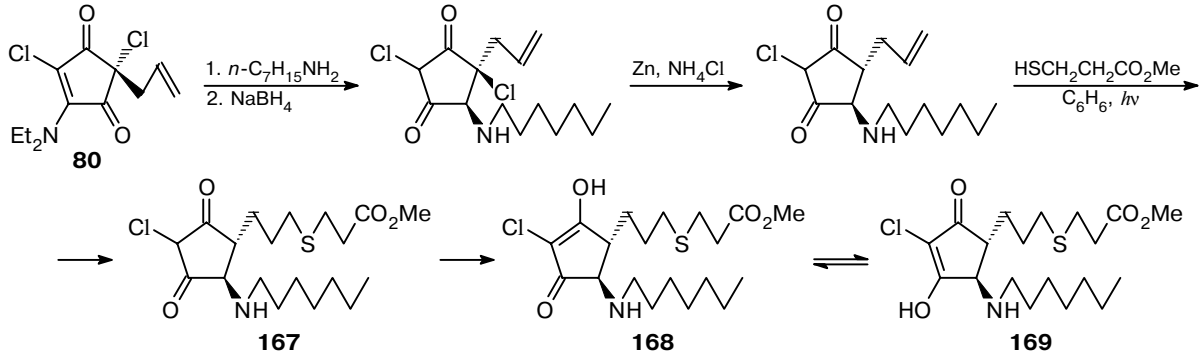
The synthesis of prostanoids of type **167**, which existed as keto-enol tautomers **168** and **169**, was described[73] (Scheme 49).

Analogs of chlorovulones containing the additional Cl atom at C(11) can find use as potential antitumor agents.[74] Dichlorocyclopentenone **53** was used in the synthesis of a 14,15-dihydro derivative of 11-chlorosubstituted chlorovulone **170** (Scheme 50).

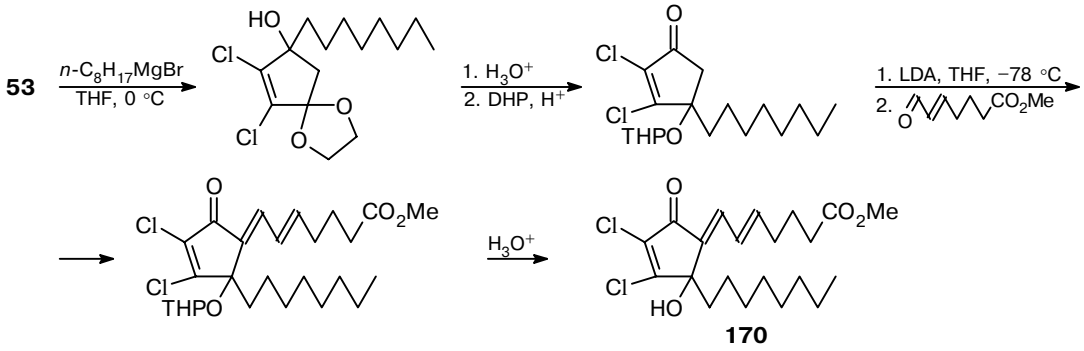
Analogously to the synthesis of compound **170**, the final stage of the synthesis of 11-chlorosubstituted chlorovulone **171** involved condensation of enolate, which was generated *in situ* from cyclopentenone **172** using LDA, with α,β-unsaturated aldehyde ester **173** giving rise to the target compound in a total yield of higher than 60% (Scheme 51).

From the aforesaid, it follows that the preparation of an original series of trichlorocyclopentenones from 5,5-tetrachlorodimethoxycyclopentadiene is essentially the development of a large synthon basis for a search for new biologically active compounds of the chlorocyclopentenone type. Numerous examples of transformations of chlorocyclopentenones and their derivatives considered in the present review are illustrative of the dynamics of the "refining" of HCCPD that can be regarded as a toxic "chlorine accumulator" and its directed conver-

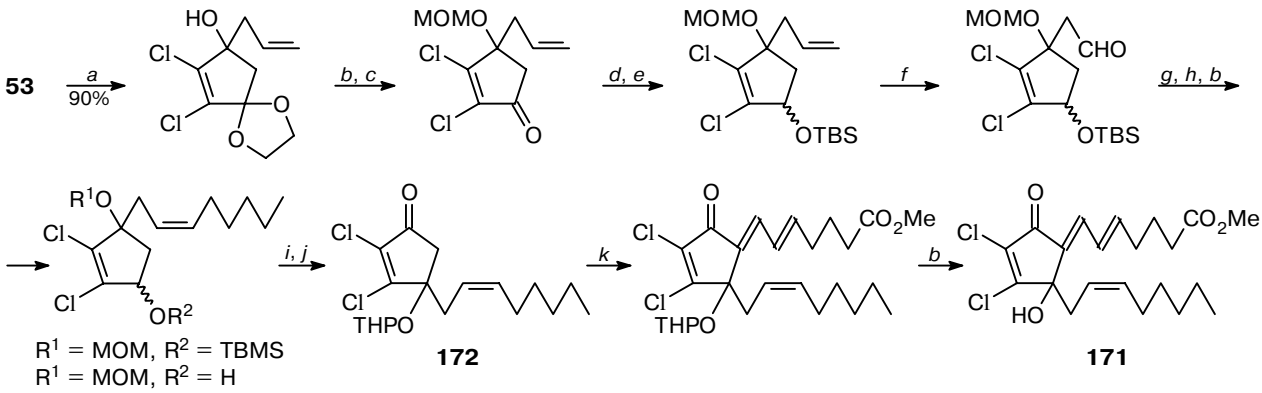
Scheme 49



Scheme 50



Scheme 51



Reagents and conditions: *a*. Zn, $BrCH_2CH{=}CH_2$; *b*. Me_2CO, H^+; *c*. Pr^i_2NEt, $ClCH_2OMe$, $ClCH_2CH_2Cl$; *d*. $NaBH_4$, EtOH, 0 °C, 1 h; *e*. Bu^tMe_2SiCl, ImH, DMF; *f*. OsO_4, $NaIO_4$; *g*. $Ph_3P{=}CH(CH_2)_4CH_3$, C_6H_6; *h*. Bu_4NF, THF; *i*. H_2CrO_4, Me_2CO; *j*. DHP, H^+; *k*. LDA, OCH—CH=CH$(CH_2)_3CO_2Me$ (**173**).

sion into the pharmacologically promising "polyheterofunctionalized state".[75,76] In these approaches, the chlorine atoms of HCCPD act as activating, directing, and binding components, thus providing the efficiency of ingenious approaches to physiologically active natural and synthetic compounds.

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References

1. H. E. Ugnade and E. T. McBee, *Chem. Rev.*, 1958, **58**, 249.
2. N. S. Zefirov, G. T. Shestakova, and M. A. Kirpichenok, *Khimiya geksakhlortsiklopentadiena i rodstvennykh soedinenii* [*Chemistry of Hexachlorocyclopentadiene and Related Compounds*], Izd. MGU, Moscow, 1985, 212 pp. (in Russian).
3. M. B. Green, G. S. Hartley, and T. F. West, *Chemicals for Crop Protection and Pest Control*, 2nd Ed., Pergamon Press, Oxford, 1979.

4. N. N. Mel´nikov, B. Ya. Libman, and P. M. Kecher, *Zh. Vsesoyuz. Khim. Obshch. im. D. I. Mendeleeva*, 1985, **30**, 268 [*Mendeleev Chem. J.*, 1985, **30** (Engl. Transl.)]
5. L. M. Korgan, *Khim. Promyshlennost'* [*Chem. Industry*]´, 1959, **5**, 78 (in Russian).
6. J. Sauer and H. Wiest, *Angew. Chem.*, 1962, **74**, 353.
7. J. Sauer and R. Sustmann, *Angew. Chem.*, 1980, **92**, 773.
8. N. S. Zefirov, in *Mechanismy geteroliticheskikh reaktsii* [*Mechanisms of Heterolytic Reactions*], Nauka, Moscow, 1976, p. 113 (in Russian).
9. M. E. Jung and J. P. Hudspeth, *J. Am. Chem. Soc.*, 1978, **100**, 4309.
10. M. E. Jung and J. P. Hudspeth, *J. Am. Chem. Soc.*, 1980, **102**, 2643.
11. Z. J. Hajos and D. R. Parrish, *J. Org. Chem.*, 1974, **39**, 1615.
12. S. A. Ismailov, Dr. Sc. (Chem.) Thesis, Ufa, 1992, 328 pp. (in Russian).
13. G. M. Strunz, A. S. Court, J. Komlossi, and M.A. Stillwell, *Can. J. Chem.*, 1969, **47**, 2087.
14. H. Nagaoka, K. Iguchi, T. Miyakoshi, N. Yamada, and Y. Yamada, *Tetrahedron Lett.*, 1986, **27**, 223.
15. B. J. Baker, R. K. Okuda, P. T. K. Yu, and P. I. Scheuer, *J. Am. Chem. Soc.*, 1985, **107**, 2976.
16. S. A. Ismailov, *Zh. Org. Khim.*, 1989, **25**, 2238 [*J. Org. Chem. USSR*, 1989, **25** (Engl. Transl.)].
17. G. A. Tolstikov, M. S. Miftakhov, Ya. L. Vel´der, and S. A. Ismailov, *Zh. Org. Khim.*, 1989, **25**, 2631 [*J. Org. Chem. USSR*, 1989, **25** (Engl. Transl.)].
18. G. A. Tolstikov, S. A. Ismailov, R. M. Khalikov, and M. S. Miftakhov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 2405 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40** (Engl. Transl.)].
19. S. A. Ismailov, M. S. Miftakhov, G. G. Balezina, Z. B. Badretdinova, and G. A. Tolstikov, *Zh. Org. Khim.*, 1991, **27**, 1885 [*J. Org. Chem. USSR*, 1991, **27** (Engl. Transl.)].
20. O. M. Kuznetsov, R. R. Akhmetvaleev, M. S. Miftakhov, and N. S. Vostrikov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 1027 [*Russ. Chem. Bull.*, 1996, **45**, 982 (Engl. Transl.)].
21. G. A. Tolstikov, S. A. Ismailov, and M. S. Miftakhov, *Zh. Org. Khim.*, 1989, **25**, 1566 [*J. Org. Chem. USSR*, 1989, **25** (Engl. Transl.)].
22. S. A. Ismailov, *Zh. Org. Khim.*, 1991, **27**, 1574 [*J. Org. Chem. USSR*, 1991, **27** (Engl. Transl.)].
23. G. A. Tolstikov, S. A. Ismailov, Ya. L. Vel´der, and M. S. Miftakhov, *Zh. Org. Khim.*, 1990, **26**, 672 [*J. Org. Chem. USSR*, 1990, **26** (Engl. Transl.)].
24. O. M. Kuznetsov, C. A. Torosyan, N. S. Vostrikov, and M. S. Miftakhov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2799 [*Russ. Chem. Bull.*, 1996, **45** (Engl. Transl.)].
25. W.-H. Chang, *Chem. Ind.*, 1965, 4744.
26. G. A. Tolstikov, S. A. Ismailov, Z. B. Badretdinova, G. G. Balezina, and M. S. Miftakhov, *Zh. Org. Khim.*, 1991, **27**, 1878 [*J. Org. Chem. USSR*, 1991, **27** (Engl. Transl.)].
27. G. A. Tolstikov, S. A. Ismailov, E. V. Prishchepova, and M. S. Miftakhov, *Zh. Org. Khim.*, 1991, **27**, 2334 [*J. Org. Chem. USSR*, 1991, **27** (Engl. Transl.)].
28. G. A. Tolstikov, S. A. Ismailov, E. V. Prishchepova, and M. S. Miftakhov, *Zh. Org. Khim.*, 1991, **27**, 2539 [*J. Org. Chem. USSR*, 1991, **27** (Engl. Transl.)].
29. S. A. Ismailov, M. S. Miftakhov, and G. A. Tolstikov, *Mendeleev Commun.*, 1991, 149.
30. M. S. Miftakhov, N. A. Ivanova, S. A. Yumagulova, S. A. Torosyan, and N. S. Vostrikov, *Zh. Org. Khim.*, 1995, **31**, 1639 [*Russ. J. Org. Chem.*, 1995, **31** (Engl. Transl.)].
31. G. A. Tolstikov, S. A. Ismailov, E. V. Prishchepova, and M. S. Miftakhov, *Zh. Org. Khim.*, 1991, **27**, 2015 [*J. Org. Chem. USSR*, 1991, **27** (Engl. Transl.)].
32. G. A. Tolstikov, S. A. Ismailov, E. V. Prishchepova, and M. S. Miftakhov, *Zh. Org. Khim.*, 1990, **26**, 2457 [*J. Org. Chem. USSR*, 1990, **26** (Engl. Transl.)].
33. G. A. Tolstikov, S. A. Ismailov, R. M. Khalikov, and M. S. Miftakhov, *Zh. Org. Khim.*, 1991, **27**, 2230 [*J. Org. Chem. USSR*, 1991, **27** (Engl. Transl.)].
34. R. R. Akhmetvaleev, N. A. Ivanova, L. R. Imaeva, T. A. Belogaeva, A. M. Shainurova, and M. S. Miftakhov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1990 [*Russ. Chem. Bull.*, 1997, **46**, 1886 (Engl. Transl.)].
35. G. A. Tolstikov, S. A. Ismailov, and M. S. Miftakhov, *Zh. Org. Khim.*, 1990, **26**, 1806 [*J. Org. Chem. USSR*, 1990, **26** (Engl. Transl.)].
36. R. R. Akhmetvaleev, T. A. Belogaeva, G. M. Karimova, and M. S. Miftakhov, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 2555 [*Russ. Chem. Bull.*, 1998, **47**, 2473 (Engl. Transl.)].
37. G. A. Tolstikov, S. A. Ismailov, R. M. Khalikov, and M. S. Miftakhov, *Zh. Org. Khim.*, 1991, **27**, 1361 [*J. Org. Chem. USSR*, 1991, **27** (Engl. Transl.)].
38. R. R. Akhmetvaleev, L. R. Imaeva, T. A. Belogaeva, and M. S. Miftakhov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1963 [*Russ. Chem. Bull.*, 1997, **46**, 2067 (Engl. Transl.)].
39. R. R. Akhmetvaleev, L. R. Imaeva, T. A. Belogaeva, and M. S. Miftakhov, *Zh. Org. Khim.*, 1999, **35**, 260 [*Russ. J. Org. Chem.*, 1999, **35** (Engl. Transl.)].
40. N. A. Ivanova, A. M. Shainurova, R. R. Akhmetvaleev, T. A. Belogaeva, and M. S. Miftakhov, *Zh. Org. Khim.*, 1999, **35**, 322 [*Russ. J. Org. Chem.*, 1999, **35** (Engl. Transl.)].
41. M. S. Miftakhov, R. M. Khalikov, R. R. Akhmetvaleev, and G. A. Tolstikov, *Zh. Org. Khim.*, 1995, **31**, 207 [*Russ. J. Org. Chem.*, 1995, **31** (Engl. Transl.)].
42. M. S. Miftakhov, R. M. Khalikov, A. A. Fatykhov, and R. R. Akhmetvaleev, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 1169 [*Russ. Chem. Bull.*,1995, **44**, 1129 (Engl. Transl.)].
43. F. A. Akbutina, S. A. Torosyan, Kh. F. Cagitdinova, and M. S. Miftakhov, *Zh. Org. Khim.*, 2000, **36**, 132 [*Russ. J. Org. Chem.*, 2000, **36** (Engl. Transl.)].
44. N. A. Ivanova, A. M. Shainurova, I. I. Furlei, and M. S. Miftakhov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2958 [*Russ. Chem. Bull.*, 1996, **45**, 2810 (Engl. Transl.)].
45. R. R. Akhmetvaleev, L. R. Imaeva, and M. S. Miftakhov, *Zh. Org. Khim.*, 1996, **32**, 1598 [*Russ. J. Org. Chem.*, 1996, **32** (Engl. Transl.)].
46. G. A. Tolstikov, M. S. Miftakhov, Ya. L. Vel´der, and S. A. Ismailov, *Zh. Org. Khim.*, 1991, **27**, 90 [*J. Org. Chem. USSR*, 1991, **27** (Engl. Transl.)].
47. R. R. Akhmetvaleev, L. R. Imaeva, and M. S. Miftakhov, *Zh. Org. Khim.*, 1997, **33**, 1342 [*Russ. J. Org. Chem.*, 1997, **33** (Engl. Transl.)].
48. N. A. Ivanova, A. M. Shainurova, and M. S. Miftakhov, *Zh. Org. Khim.*, 2000, **36**, 452 [*Russ. J. Org. Chem.*, 2000, **36** (Engl. Transl.)].
49. N. A. Ivanova, A. M. Shainurova, L. V. Spirikhin, and M. S. Miftakhov, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 2552 [*Russ. Chem. Bull.*, 1998, **47**, 2469 (Engl. Transl.)].
50. G. A. Tolstikov, M. S. Miftakhov, Ya. L. Vel´der, and S. A. Ismailov, *Zh. Org. Khim.*, 1991, **27**, 83 [*J. Org. Chem. USSR*, 1991, **27** (Engl. Transl.)].
51. L. F. Chertanova, S. A. Ismailov, L. M. Khalilov, M. S. Miftakhov, E. V. Prishchepova, O. V. Shitikova, and G. A. Tolstikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, 1794 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1991, **40** (Engl. Transl.)].

52. R. R. Akhmetvaleev, L. R. Imaeva, T. A. Belogaeva, and M. S. Miftakhov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1699 [*Russ. Chem. Bull.*, 1997, **46**, 1622 (Engl. Transl.)].
53. R. R. Akhmetvaleev, Dr. Sc. (Chem.) Thesis, Institute of Organic Chemistry of the Ufa Research Center of the Russian Academy of Sciences, Ufa, 2000, 345 pp. (in Russian).
54. F. A. Akbutina, S. A. Torosyan, and M. S. Miftakhov, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1660 [*Russ. Chem. Bull.*, 1998, **47**, 1616 (Engl. Transl.)].
55. F. A. Akbutina, S. A. Torosyan, E. M. Vyrypaev, I. N. Furlei, and M. S. Miftakhov, *Zh. Org. Khim.*, 1999, **35**, 1414 [*Russ. J. Org. Chem.*, 1999, **35** (Engl. Transl.)].
56. N. S. Vostrikov, S. A. Torosyan, F. A. Akbutina, E. M. Vyrypaev, L. V. Spirikhin, and M. S. Miftakhov, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 343 [*Russ. Chem. Bull.*, 1999, **48**, 342 (Engl. Transl.)].
57. N. S. Vostrikov, S. A. Torosyan, F. A. Akbutina, E. M. Vyrypaev, and M. S. Miftakhov, *Zh. Org. Khim.*, 1999, **35**, 651 [*Russ. J. Org. Chem.*, 1999, **35** (Engl. Transl.)].
58. S. A. Torosyan, Ph. D. (Chem.) Thesis, Ufa, 2000 (in Russian).
59. G. A. Tolstikov, R. M. Khalikov, S. A. Ismailov, R. R. Akhmetvaleev, and M. S. Miftakhov, *Zh. Org. Khim.*, 1993, **29**, 342 [*Russ. J. Org. Chem.*, 1993, **29** (Engl. Transl.)].
60. L. F. Chertanova, F. A. Akbutina, S. A. Torosyan, L. M. Khalilov, and M. S. Miftakhov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1979 [*Russ. Chem. Bull.*, 1997, **46**, 1875 (Engl. Transl.)].
61. F. A. Akbutina, S. A. Torosyan, N. S. Vostrikov, L. V. Spirikhin, and M. S. Miftakhov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2961 [*Russ. Chem. Bull.*, 1996, **45**, 2813 (Engl. Transl.)].
62. G. A. Tolstikov, S. A. Ismailov, and M. S. Miftakhov, *Zh. Org. Khim.*, 1991, **27**, 2547 [*J. Org. Chem. USSR*, 1991, **27** (Engl. Transl.)].
63. F. A. Akbutina, S. A. Torosyan, and M. S. Miftakhov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1646 [*Russ. Chem. Bull.*, 1997, **46**, 1569 (Engl. Transl.)].
64. M. Gill and R. W. Rickards, *Chem. Commun.*, 1979, **3**, 121.
65. J. R. Behing, K. A. Babiak, J. S. Ng, and A. L. Campbill, *J. Am. Chem. Soc.*, 1988, **110**, 2641.
66. P. W. Collins and S. W. Djuric, *Chem. Rev.*, 1993, **93**, 1533.
67. R. R. Akhmetvaleev, G. M. Baibulatova, O. M. Kuznetsov, and M. S. Miftakhov, *Zh. Org. Khim.*, 2000, **36**, 450 [*Russ. J. Org. Chem.*, 2000, **36** (Engl. Transl.)].
68. R. E. Donaldson and P. L. Fuchs, *J. Am. Chem. Soc.*, 1981, **103**, 2108.
69. R. E. Donaldson, J. C. Saddler, S. Byrn, A. T. McKenzie, and P. L. Kuchs, *J. Org. Chem.*, 1983, **48**, 2167.
70. C. R. Johnson and T. D. Pennig, *J. Am. Chem. Soc.*, 1988, **110**, 4726.
71. R. R. Akhmetvaleev, G. M. Baibulatova, G. A. Shavaleeva, and M. S. Miftakhov, *Zh. Org. Khim.*, 2001, **37**, 51 [*Russ. J. Org. Chem.*, 2001, **37** (Engl. Transl.)].
72. M. E. Adler, S. A. Yumagulova, S. A. Torosyan, and M. S. Miftakhov, *Zh. Org. Khim.*, 1994, **30**, 943 [*Russ. J. Org. Chem.*, 1994, **30** (Engl. Transl.)].
73. G. A. Tolstikov, S. A. Ismailov, E. V. Prishchepova, L. M. Khalilov, O. V. Shitikova, and M. S. Miftakhov, *Zh. Org. Khim.*, 1991, **27**, 2254 [*J. Org. Chem. USSR*, 1991, **27** (Engl. Transl.)].
74. R. R. Akhmetvaleev, G. M. Baibulatova, I. F. Nuriev, and M. S. Miftakhov *Zh. Org. Khim.*, 2001, **37**, 1138 [*Russ. J. Org. Chem.*, 2001, **37** (Engl. Transl.)].
75. Pat. RU 2144767; *Byul. Izobr.*, 2000, 3, 2 pp. (in Russian).
76. Pat. RU 2145166; *Byul. Izobr.*, 2000, 4, 2 pp. (in Russian).

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