Structure-dependent transformations of the tetrachlorocyclopentadienone dimer and the product of its substitutive rearrangement in reactions with $NaBH_4$, $CrCl_2$, $LiAlH_4$, and Zn

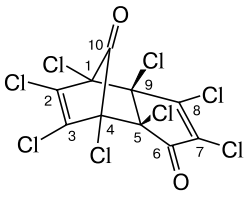
*F. A. Gimalova, O. A. Gavrilov, and M. S. Miftakhov**

Institute of Organic Chemistry, Ufa Research Center of the Russian Academy of Sciences, 71 prosp. Oktyabrya, 450054 Ufa, Russian Federation. Fax: +7 (347 2) 35 6066. E-mail: bioreg@anrb.ru

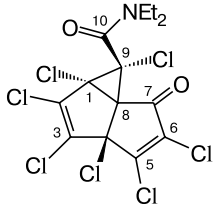
Dechlorination of the tetrachlorocyclopentadienone dimer and perchloro-7-oxotricyclo[6.1.0.0^{4,8}]nona-2,5-diene-9-carboxylic acid *N*,*N*-diethylamide with hydride ion donors ($NaBH_4$, $LiAlH_4$, *etc.*) and electron donors ($CrCl_2$ or Zn) were studied. The possible pathways of unusual transformations of both sterically hindered molecules are considered.

Key words: tetrachlorocyclopentadienone dimer, cyclopropanes, tricyclic compounds, reduction, dechlorination, reductive dimerization, aromatization, organochlorine compounds.

The reactions of the 2,3,4,5-tetrachlorocyclopentadienone dimer (**1**)[1] are poorly studied.[2,3] Recently, we have found a new reaction of diketone **1** with primary and secondary amines[4] giving rise to unsaturated hetpachloro-substituted amidoketones with the tricyclo[6.1.0.0^{4,8}]nonane skeleton, for example, to tricyclic compound **2** containing the cyclopropanecarboxylic acid fragment. Sterically crowded polyfunctional tricyclic compounds with molecular cores **1** and **2** are of interest primarily because their chemical behavior is unpredictable, which opens a route to nontrivial structures.



1

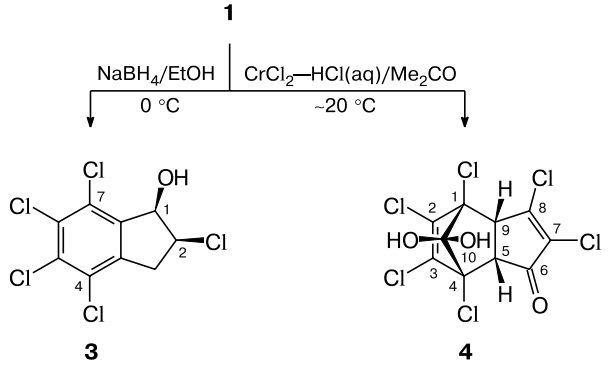


2

In the present study, we examined reactions of compounds **1** and **2** with available reducing agents, such as $NaBH_4$, $CrCl_2$, $LiAlH_4$, and Zn.

Reductive transformations of tricyclic compound 1. The reaction of diketone **1** with $NaBH_4$ in ethanol proceeds as reductive decarbonylation accompanied by aromatization even at 0 °C to give 1-hydroxy-2,4,5,6,7-pentachloroindane (**3**), whereas reduction of compound **1** with chromium dichloride in an acidic acetone—water mixture at ~20 °C occurs without destruction of the skeleton as selective dechlorination of the C(5) and C(9) atoms accompanied by hydration of the bridging C=O group. This transformation product **4** appeared to be stable *gem*-diol (Scheme 1).

Scheme 1

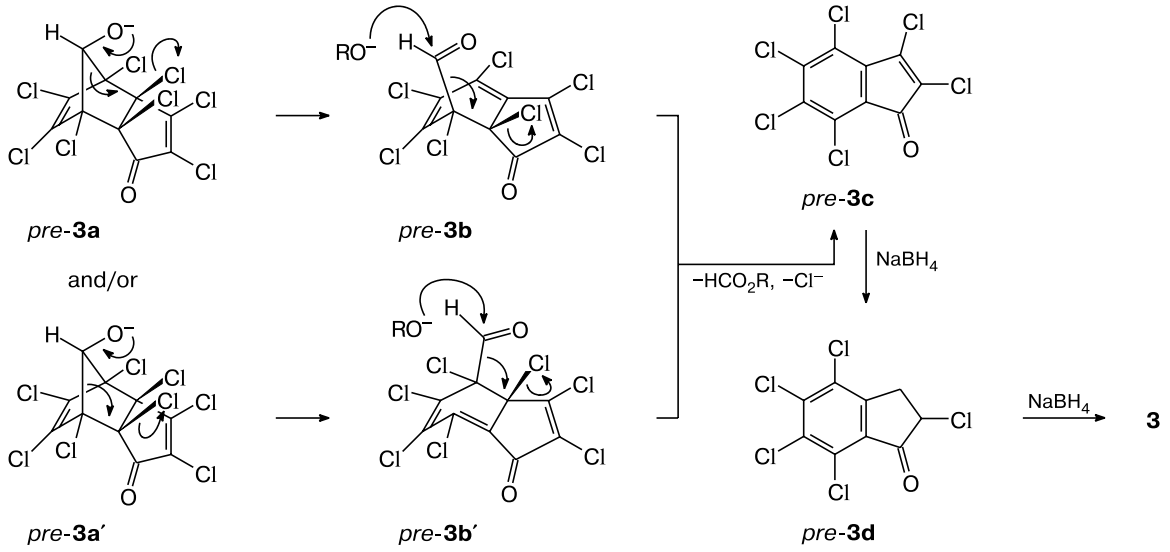


In the ^1H NMR spectrum of *cis*-chlorohydrin **3**, a doublet of the C<u>H</u>OH group at δ 5.28 with $J_{1,2}$ = 5.1 Hz is the key signal for the determination of the configuration of this compound (*cf.* lit. data[5]). The characteristic feature of the transformation **1** → **3** is that the decarbonylation—aromatization tandem occurs in the $NaBH_4$/EtOH system even at 0 °C, whereas norbornen-7-one derivatives similar to bicyclic compound **1** efficiently undergo decarbonylation under rather drastic thermolysis conditions (~160 °C).[6]

The possible stepwise pathway of aromatization of diketone **1** is presented in Scheme 2. The structure of the

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1001—1007, June, 2006.

Scheme 2



oxanion generated upon the addition of the $[BH_4]^-$ anion to the bridging keto group of diketone **1** can readily undergo the Grobs fragmentation[7] accompanied by concerted cleavage of three bonds through any one of two transition states (conventionally, through anions *pre*-**3a** and *pre*-**3a**′).* This gives rise to isomeric aldehydes *pre*-**3b** and *pre*-**3b**′, which are decomposed in a weakly basic medium to form indenone *pre*-**3c**. Reduction of ketone *pre*-**3c** with an excess of $NaBH_4$ involves the nucleophilic displacement of the chlorine atom at the C(3) atom with a hydride ion as the first step followed by the 1,4-addition of the H^- ion (from $[BH_4]^-$) to intermediate 2-chloro enone (chemistry of β-chlorovinyl ketones was described in Ref. 8).

The final step of transformations involves reduction of chloro ketone *pre*-**3d**, which occurs with high *cis*-stereoselectivity because the bulky chlorine atom at the α position with respect to the keto group hinders the approach of the $[BH_4]^-$ anion from the side occupied by the chlorine atom.

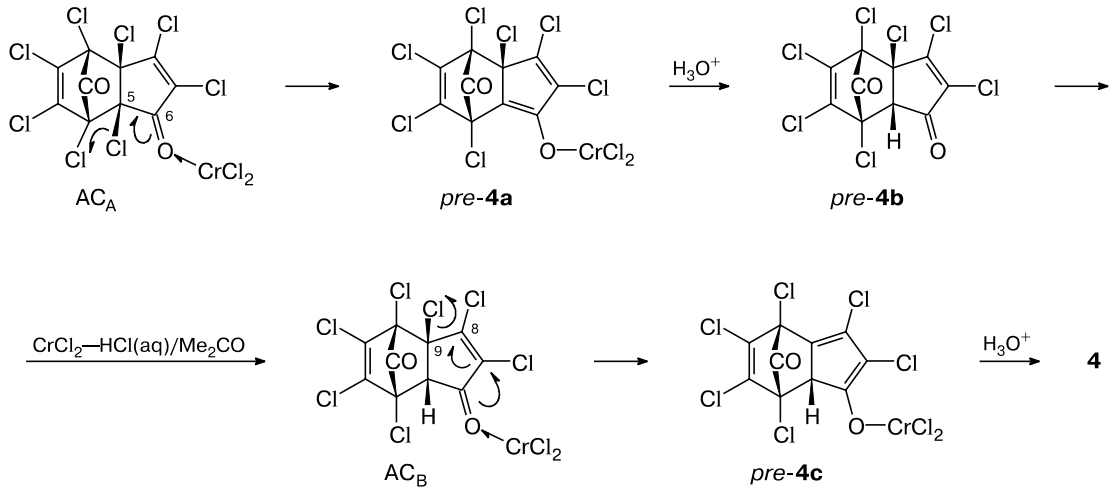
The mechanism of formation of compound **4** in the reaction of diketone **1** with chromium(II) dichloride in an acidic aqueous organic medium is also of interest. Of four chlorine atoms bound to the sp^3-hybridized C(1), C(4), C(5), and C(9) atoms in molecule **1**, reductive chlorine removal with $CrCl_2$ (an efficient reagent for dehalogenation of α-halo ketones[9]) occurs only at the C(5) and C(9) atoms. Reaction product **4** derived from diketone **1** by dechlorination at the C(5) and C(9) atoms and hydration at the C(10) atom was isolated in the chemically pure state by chromatography on a silica gel column. The IR spectrum of compound **4** shows a band at 3400 cm^{-1} (OH). The ^{13}C NMR spectrum of this compound has a characteristic signal for the *gem*-dihydroxylated carbon atom at δ_C 112.21. The ^1H NMR spectrum of compound **4** shows two singlets for the hydroxy hydrogen atoms at δ_H 6.98 and 7.37.

Apparently, hydration of the bridging C=O group and stability of the hydrate result from internal hindrance of molecules **1** and **4** and the presence of the electronegative chlorine atoms at the C(1) and C(4) atoms. The inactivity of these chlorine atoms with respect to $CrCl_2$ is attributed to the fact that these atoms cannot be eliminated by reductive enolization of the Cl—CH—C=O fragments initiated by the approach of the $CrCl_2$ molecule to the bridging keto group (Bredt's rule). At the same time, the replacement of the chlorine atoms at the C(5) and C(9) atoms with H atoms is not forbidden according to Bredt' rule and, consequently, this process occurs in satisfactory yield.

Selective dechlorination of ketone **1** with $CrCl_2$ is consistent with the known data on the nature and mechanism of action of this inorganic radical cation.[10,11] The electronegativity of the oxygen atom is higher than that of the chlorine atom (4.0 and 3.5 $eV^{1/2}$, respectively)[12] and the formation of the $O—Cr^{III}$ covalent bond is more probable than the formation of the $Cl—Cr^{III}$ bond. It should be noted that $CrCl_2$ reduces α-chloro ketones according to the scheme of chlorine removal assisted by enolization, whereas the Cl(1) and Cl(4) atoms cannot be removed from molecule **1**. However, this process can occur for the C(5)—Cl and C(9)—Cl bonds through the activated AC_A

* Hereinafter, the intermediates, whose presence was not experimentally established, are denoted in the schemes and in the text by the numbers corresponding to the codes of the final products with the addition of the prefix *pre* and the suffix (**a**, **b**, **c**, *etc.*), the latter indicating the order of formation of the intermediates.

Scheme 3



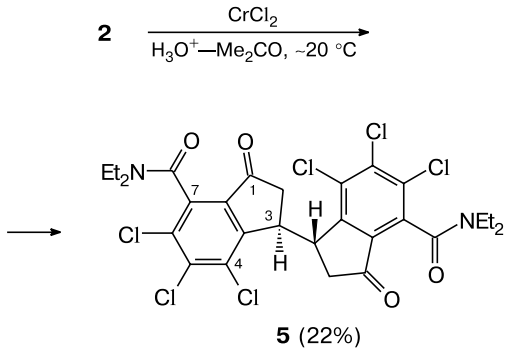
and AC$_B$ complexes (the sequence of the events is not important) and enolates *pre*-**4a** and *pre*-**4c** (Scheme 3).*

Protonation of the C=C bonds in dienolates *pre*-**4a** and *pre*-**4c** occurs only from the β region. Protonation from the α region, which could give rise to the *trans*-fused intermediate, is thermodynamically impossible.

Reductive transformations of tricyclic compound 2. Dechlorination of tricyclic compound **2** in the CrCl$_2$—HCl(aq)/Me$_2$CO system unexpectedly afforded dimer **5** (Scheme 4).

The structure of compound **5** was established by NMR spectroscopy and mass spectrometry. The ^{13}C NMR spectrum shows signals of the symmetrical CH (δ_C 37.68) and CH$_2$ groups (δ_C 37.65) and one signal for the C atoms of the nonconjugated keto groups (δ_C 199.51). Strong steric hindrance in molecule **5** is manifested in the ^{1}H NMR spectrum, where the signals for the protons of each N(CH$_2$Me)$_2$ group are nonequivalent. The constant ^2J for the CH$_2$ protons in the cyclopentanone fragment is abnormally high (19.5 Hz) and is closer to ^2J for strained bornan-2-ones (^2J = 18.4 Hz, see Ref. 13) than to ^2J in

Scheme 4



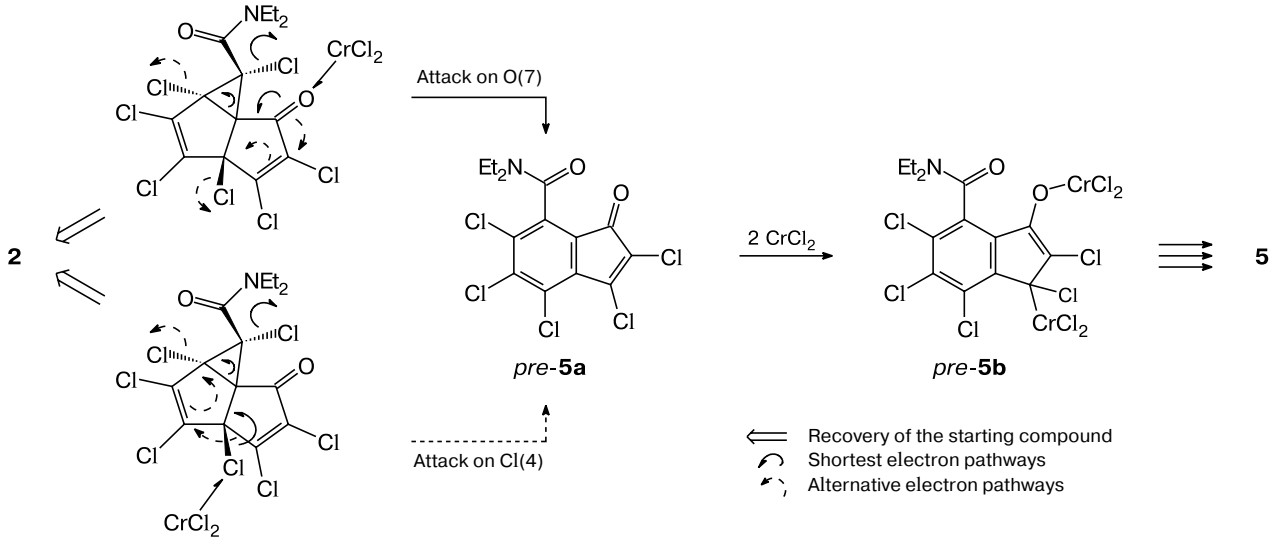
the spectra of cyclopentanones. In the mass spectrum of dimer **5**, the isotope cluster of the molecular ion peak corresponds to six chlorine atoms; there is also a cluster peak at $m/z = 1/2\ M$ whose appearance is characteristic of three chlorine atoms. This is indicative of decomposition of structure **5** giving rise to two monomeric fragments.

The probable pathways of the formation of compound **5** are shown in Scheme 5.* The rates of the reaction of CrCl$_2$ with lower organohalides[11] provide evidence that the chlorine atom at the doubly allylic C(4) atom in tricyclic compound **2** may be most susceptible to the attack. However, the calculated charges of these atoms are low. At the same time, calculations of the partial charges in amidoketone **2** demonstrated that the negative charge of the oxygen atom at the C(7) atom is substantially higher than those of the chlorine atoms (see below). Hence, the

* The transformation of one C(sp^3)—Cl bond of organohalide into the C—H bond under the action of CrCl$_2$ in an acidic proton-donor medium involves the following steps:[10,11] (1) one-electron transfer from the CrCl$_2$ molecule to the C—Cl bond of organohalide; (2) migration of the resulting C radical to the Cr^{III} atom accompanied by the repeated one-electron transfer from the second CrCl$_2$ molecule through the bridging halide anion; (3) decomposition of the dinuclear complex; and (4) Cr—C bond protolysis in the organylchromium(III) intermediate that is eliminated. Theoretically, two CrCl$_2$ molecules (in practice, their number is larger) are consumed in one event of reductive dechlorination. After each cycle, the starting atomic group accepts two electrons. For simplicity, the starting attack of CrCl$_2$ followed by the rearrangement of the bonds in the molecule can arbitrarily be considered as the electron pair transfer of the same type.

* The starting one-electron attack of CrCl$_2$ on molecule **2** followed by the one-electron transfer from the second CrCl$_2$ molecule are denoted by the same "arrow-hook" sign. The formation of intermediate *pre*-**5b** requires at least two CrCl$_2$ molecules (for comparison, see Scheme 3).

Scheme 5



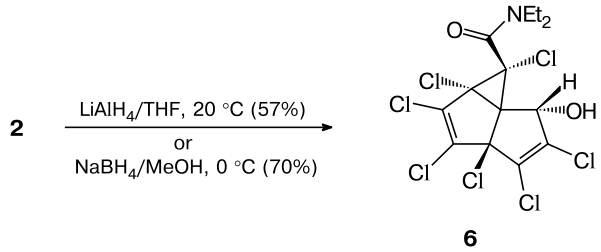
attack of $CrCl_2$ most likely starts from the coordination and redox mutation of the Cr^{II} cation and the C=O group. In any event, one-electron reduction of molecule **2** initiates interrelated processes of the cyclopropane ring opening and leaving of two chlorine atoms from the C(4) and C(9) atoms to form indenone structure *pre*-**5a**.

The subsequent one-electron transfer from $CrCl_2$ to intermediate *pre*-**5a** and the new C—Cr^{III} bond formation can give rise to organochromium intermediates of *pre*-**5b** type, which are similar in genesis to both aryl radical anions in the Birch reaction[14] and Cr^{III} organyl intermediates in the Nozaki—Hiyama reaction.[15] Cross-coupling of β-chlorovinyl ketone *pre*-**5a** with intermediate *pre*-**5b** followed by reduction of the C(sp^3)—Cl bonds affords didehydro dimer **5**. In spite of the fact that the rate of C—Cr^{III} bond protolysis in an acidic acetone—water mixture is high, product **5** was obtained in surprisingly high yield.

The reactions of hydride ion donors, *viz.*, $NaBH_4$/MeOH or $LiAlH_4$/THF, with compound **2** at 0 and 20 °C, respectively, (Scheme 6) proceed slowly and afford only one of two possible alcohols (presumably, 7α-epimer **6**). The reactions of other hydride reagents with amidoketone **2** invariably produce either alcohol **6** (in the $NaBH_4$—$CeCl_3$/MeOH, $NaBH_3CN$/MeOH—AcOH, or $Zn[BH_4]_2/Et_2O$ systems) or products of extensive decomposition (in the lithium selectride/THF system). Attempts to invert the configuration of alcohol **6** at the C(7) atom under the forced conditions of the Mitsunobu reaction[16] gave exclusively the starting alcohol.

High stereoselectivity of reduction of amidoketone **2** can be traditionally attributed to the steric control and the attack of the reagent from the more readily accessible side

Scheme 6



of the bicyclo[3.3.0]octane fragment of the molecule. However, the absence of the second epimer (presumably, 7β) makes it difficult to determine the configuration of alcohol **6** containing no other hydrogen atoms in the vicinity of the CHOH group by spectroscopic methods.

The α-orientation of the OH group in alcohol **6** was assumed based on the analysis of the published data[17—19] on stereoselectivity of the addition of various reagents at the π bonds of bicyclo[3.3.0]octane derivatives and their analogs. In these systems, the bond angles between the five-membered rings vary in the range of 115—130°. The C(3)—C(4)—C(5) and C(1)—C(8)—C(7) angles in tricyclic compound **2** calculated by the MM2 method are 116.04 and 126.1°, respectively. The corresponding angles in the closest analog of diethylamide **2**, *viz.*, morpholide containing the identical acyl substituent,[4] are 117.41 and 122.20° (X-ray diffraction data). Generally, the addition of reagents to such molecules occurs from the "outer side of the open cardboard" even in the presence of blocking substituents adjacent to the reaction center.

In the absence of X-ray diffraction data on the structure of alcohol **6**, the conclusion about the α orientation of the OH group can be supported by the following fact.

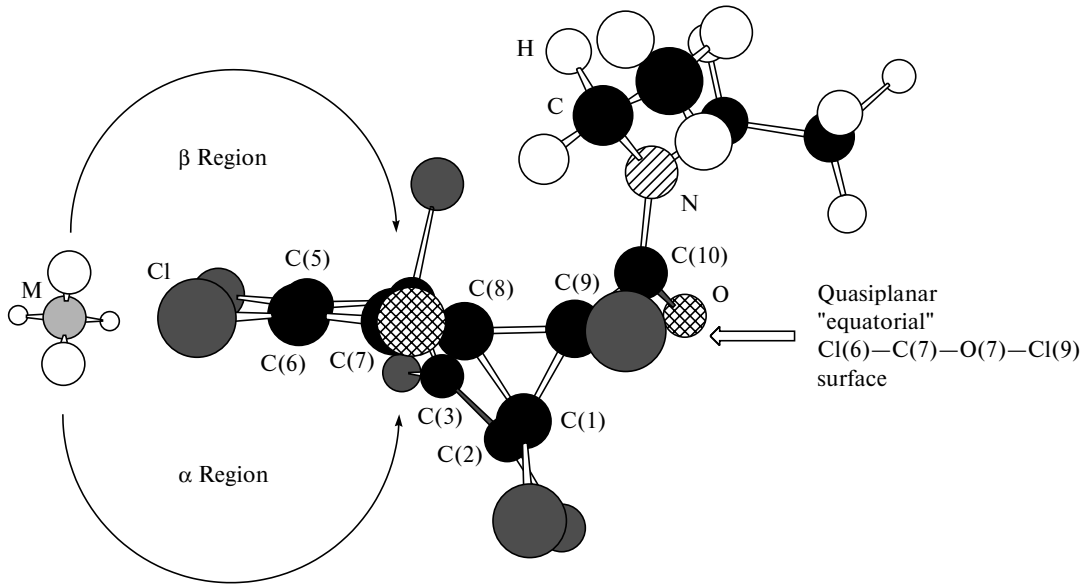


Fig. 1. Visualization of the probabilities of the formation of α-alcohol **6** or its 7β-epimer (*epi*-**6**) when the tetrahedral $[M^{III}H_4]^-$ anions (M = B or Al) approach the keto group of amidoketone **2** taking into account the steric and electrostatic effects.

Table 1. Calculated* atomic partial charges in tricyclic amidoketone **2** (principal charges are printed in semibold face)

Atom	Method *A*	Method *B*
C(1)	0.181	–0.072
C(2), C(6)	–0.042, –0.086	–0.138, –0.273
C(3), C(5)	–0.041, 0.128	–0.234, –0.184
C(4)	0.122	0.067
C(7)	**0.311**	**0.413**
C(8)	–0.007	–0.231
C(9)	0.125	–0.124
C(10)	**0.345**	**0.316**
$N(\underline{C}H_2CH_3)_2$	0.029, 0.025	–0.187, –0.199
$N(CH_2\underline{C}H_3)_2$	–0.133, –0.135	–0.342, –0.340
N	0.333	–0.071
C(7)<u>O</u>	**–0.696**	**–0.262**
C(10)<u>O</u>	**–0.841**	**–0.366**
C(2)<u>Cl</u>, C(6)<u>Cl</u>	0.020, 0.030	0.178, 0.195
C(5)<u>Cl</u>, C(3)<u>Cl</u>	**0.115**, 0.033	**0.182**, 0.168
C(1)<u>Cl</u>	–0.061	0.112
C(4)<u>Cl</u>	–0.067	0.029
C(7)<u>Cl</u>	–0.040	0.097
$N(C\underline{H}_2CH_3)_2$	0.027, 0.030	0.123, 0.129, 0.141, 0.148
$N(CH_2C\underline{H}_3)_2$	0.040, 0.037	0.109, 0.116, 0.117, 0.124, 0.135

* Calculations of the partial charges by the extended Hückel method (*A*) and the Mulliken method (*B*). The data for the atoms similar in topology and charges are given in pairs.

Table 2. Scalar sums of the charges in three regions of molecule **2**[a]

Region	Total atomic charge		Difference in the total charges of nonequatorial atoms (β – α)
	A[b]	*B*[b]	
Upper (β)	0.745	0.465	0.645 (*A*), 0.158 (*B*)
Lower (α)	0.100	0.307	—
Quasiplanar "equatorial" surface[c]	–0.984 (~86%)	–0.863 (89.5%)	—

[a] The conventionally upper (β) and lower (α) atomic groups are located outside the quasiplanar ("equatorial") interlayer (see Fig. 1).
[b] The initial calculation method (see Table 1).
[c] The correspondence to the charge parity of the molecule is given in parentheses (+/–).

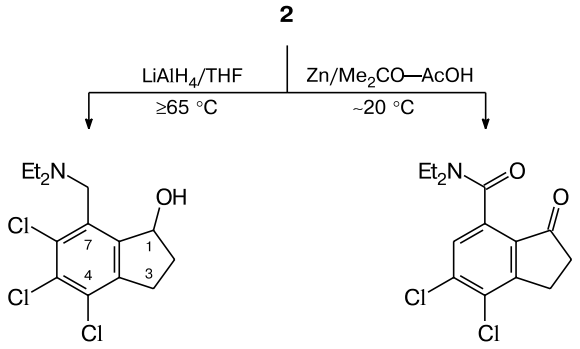
An analysis of the structure of the starting amidoketone **2** by the MM2 method and computer calculations of all atomic partial charges in the molecule revealed an ensemble of C, O, and Cl atoms, which are adjacent to the keto group, lie on the common quasiplanar surface, and bear a total negative charge. Calculations of the charges of the atoms conventionally located above (β region) and below (α region) this interlayer (the equator of the molecule) demonstrated that the total positive charge in the β region is substantially higher than that in the α region (Fig. 1, Tables 1 and 2).* As the ion pair of the complex hydride moves toward the plane of the oxo group of the

* The calculations of the molecular parameters of compounds **1** and **2** by the MM2 method and the atomic partial charges were kindly performed by one of the referees of the present paper in the course of discussion.

ketone, the [MH_4] anion essential for the reaction is attracted predominantly to the β region. Hence, the probability of the attack on the keto group from this side increases, resulting in the predominant formation of α-alcohol.

Reductive dechlorination of ketoamide **2** in the $LiAlH_4$/THF system at ≥65 °C affords amino alcohol **7**, which corresponds to more complete reduction of the cyclopentenone fragment, fusion and aromatization of two other rings, and the transformation of the amide into tertiary amine (Scheme 7).

Scheme 7



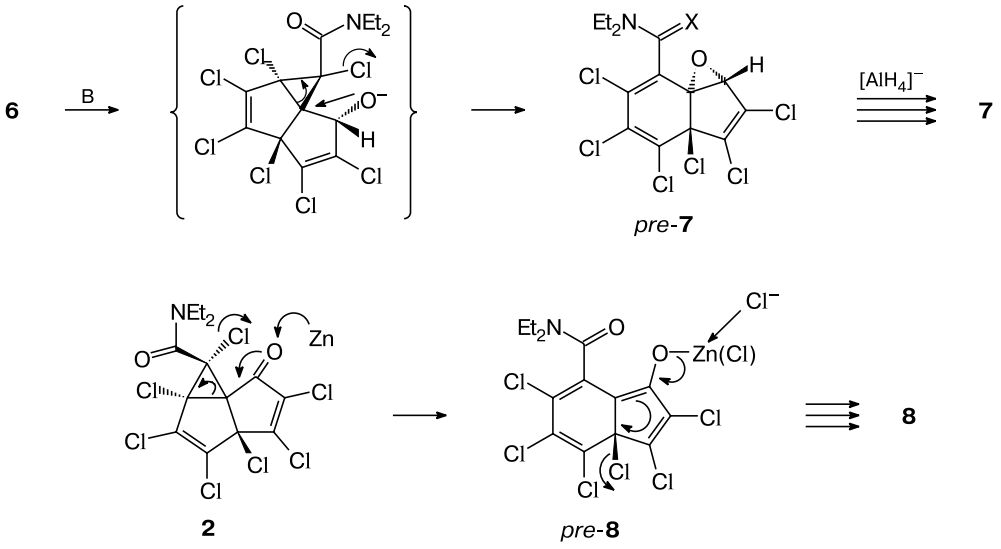
7 (~45%) **8** (77%)

Ketoamide **2** undergoes analogous aromatization accompanied by partial reductive dechlorination upon storage in the Zn/Me_2CO—AcOH system. This reaction produces only *vic*-dichloro-substituted ketoamide **8**, although this degree of dechlorination can give rise to two other regioisomers (4,6- and 5,6-dichloro-substituted) containing the same molecular skeleton. The structure of product **8** was established by mass spectrometry, ^1H and ^{13}C NMR spectroscopy, and also based on the analysis of the possible pathways of its formation (taking into account the nonactivated chlorine atoms of the vinyl fragment of compound **2**, which are inert toward Zn). The structure of **8** was confirmed by comparing the calculated chemical shifts in the ^{13}C and ^1H NMR spectra of ketoamide **8** and two its regioisomers with the use of the ACD-Labs computer program. The close agreement between the calculated chemical shifts δ_C and δ_H and the corresponding experimental values was observed only for compound **8**.

Intermediates *pre*-**7** and *pre*-**8** can serve as precursors of 4,5,6-trichloro-7-(*N*,*N*-diethylamino)methylindan-1-ol (**7**) and 4,5-dichloro-7-diethylaminocarbonylindan-1-one (**8**), respectively. The formation of these intermediates is facilitated by the intramolecular assistance of the β-oxy or oxo function to the cleavage of the cyclopropane fragment in amidoketone **2** (Scheme 8).

On the whole, as mentioned above, the above-considered transformations of compounds **1** and **2** are nontrivial examples of the dependence of the reactions of externally similar sterically crowded molecules on their structural features. Fine differences in the pathways of the reductive reactions involving hydride ion donors and electron donors are aslo of interest.

Scheme 8



X = O, H_2

B is a base (an excess of $LiAlH_4$, impurities of alkalis or alkoxides in complex hydride, *etc.*)

Experimental

The IR spectra were recorded on UR-20 and Specord M-80 spectrometers in Nujol mulls. The NMR spectra were measured on a Bruker AM-300 spectrometer (300.13 for ^{1}H and 75.47 MHz for ^{13}C). The mass spectra were obtained on a Thermo Finnigan MAT 95XP instrument (70 eV, the ionization temperature was 200 °C, the inlet temperature was 5—270 °C, and the temperature rise rate was 22 °C min^{-1}). The course of the reactions was monitored by TLC on Silufol UV 254:366 plates; the spots were visualized by burning or exposure to iodine vapor. The products were isolated by silica gel column chromatography (30—60 g of the adsorbent per gram of the substance) with the use of freshly distilled solvents as the eluent. The starting compounds **1** and **2** were prepared according to procedures described earlier.[1,4]

(1*R,2*S**)-2,4,5,6,7-Pentachloroindan-1-ol (3).** A solution of diketone **1** (0.52 g, 1.19 mmol) in EtOH (5 mL) was added dropwise to a stirred suspension of 85% $NaBH_4$ (0.26 g, 5.85 mmol) in ethanol (5 mL) at 0 °C. The reaction mixture was stirred at 22±2 °C for 1 h (TLC control). An excess of $NaBH_4$ was quenched with water, ethanol and the volatiles were evaporated, and the residue was extracted with ethyl acetate (3×30 mL). The combined organic extracts were dried with $MgSO_4$ and concentrated. The residue was chromatographed on a silica gel column (AcOEt—petroleum ether, 1 : 1, as the eluent). Compound **3** was isolated as white crystals in a yield of 0.26 g (71%), m.p. 156—158 °C. IR, ν/cm^{-1}: 766, 868, 1018, 1096, 1156, 1174, 1384, 1558, 3448. ^{1}H NMR (acetone-d_6), δ: 3.28 (dd, 1 H, C$\underline{H}_A$H$_B$, ^2J = −16.5 Hz, ^3J = 8.2 Hz); 3.55 (dd, 1 H, CH$_A\underline{H}_B$, ^2J = −16.5 Hz, ^3J = 7.2 Hz); 4.75 (m, 1 H, CHCl); 5.11 (br.s, 1 H, OH); 5.28 (d, 1 H, OCH, J = 5.1 Hz). ^{13}C NMR, δ: 40.01 (C(3)); 59.49 (C(2)); 75.19 (C(1)); 128.38, 129.74, 130.92, 132.12 (C(5), C(3a), C(4), C(7)); 140.55, 141.61 (C(6), C(7a)). MS, *m/z*: 304, 306, 308, 310, 312 [M]$^+$; 269, 271, 273, 275 [M − Cl]$^+$; 234, 236 [M − 2 Cl]$^+$.

(1*S,4*S**,5*R**,9*S**)-1,2,3,4,7,8-Hexachloro-10,10-dihydroxytricyclo[5.2.1.0^{5,9}]deca-2,7-dien-6-one (4).** An acidic 10% aqueous $CrCl_2$ solution (30 mL), which was prepared according to a known procedure,[9] was gradually added to a stirred solution of compound **1** (0.5 g, 1.15 mmol) in Me_2CO (10 mL) at 22±2 °C. The reaction mixture was stirred for 30 min, acetone was evaporated, and the aqueous phase was extracted with $CHCl_3$ (3×30 mL). The combined extracts were washed with a saturated NaCl solution, dried with $MgSO_4$, and concentrated. The residue was purified by chromatography on a silica gel column (AcOEt—petroleum ether, 1 : 1, as the eluent), and compound **4** was obtained as colorless crystals in a yield of 0.15 g (~34%), m.p. 101—103 °C. Found (%): C, 30.97; H, 1.20; Cl, 54.42. $C_{10}H_4Cl_6O_3$. Calculated (%): C, 31.41; H, 1.04; Cl, 54.97. IR, ν/cm^{-1}: 1582, 1714, 3400. ^{1}H NMR (acetone-d_6), δ: 3.65 (d, 1 H, H(9), J = 6.1 Hz); 4.12 (d, 1 H, H(5), J = 6.1 Hz); 6.98 and 7.37 (both s, 1 H each, OH). ^{13}C NMR, δ: 55.57 (C(9)); 55.63 (C(5)); 75.87, 77.41 (C(1), C(4)); 112.21 (C(10)); 127.93, 128.13 (C(2), C(3)); 135.67 (C(7)); 159.16 (C(8)); 190.09 (C(6)).

(3*R,3′*S**)-3,3′-Bis(4,5,6-trichloro-7-diethylaminocarbonylindan-1-one) (5)** was prepared analogously to compound **4** starting from compound **2** (0.5 g, 1.08 mmol). The yield was 0.15 g (22%), m.p. 271—273 °C. Found (%): C, 50.90; H, 3.90; Cl, 31.34; N, 4.00. $C_{28}H_{26}Cl_6N_2O_4$. Calculated (%): C, 50.40; H, 3.93; Cl, 31.88; N, 4.20. IR, ν/cm^{-1}: 1072, 1192, 1378, 1462, 1732. ^{1}H NMR ($CDCl_3$), δ: 1.11 and 1.34 (both t, 6 H each, Me, J = 7.1 Hz); 1.72 (d, 2 H, 2 C$\underline{H}_A$H$_B$, J = −19.5 Hz); 2.58 (dd, 2 H, 2 CH$_A\underline{H}_B$, ^2J = −19.5 Hz, ^3J = 7.9 Hz); 3.10 and 3.13 (both dq, 2 H each, 2 NC$\underline{H}_A$H$_B$, ^2J = −14.2 Hz, ^3J = 7.1 Hz); 3.58 and 3.74 (both dq, 2 H each, 2 NCH$_A\underline{H}_B$, ^2J = −14.2 Hz, ^3J = 7.1 Hz); 4.66 (d, 2 H, H(3), J = 7.3 Hz). ^{13}C NMR, δ: 12.19, 13.68 (Me); 37.65 (C(2)); 37.68 (C(3)); 39.17, 42.94 (NCH_2); 132.19, 132.41, 133.52, 133.61 (C(3a), C(7), C(6), C(5)); 139.83 (C(4)); 151.81 (C(7a)); 162.98 (N—C=O); 199.51 (C(1)). MS, *m/z*: 664, 666, 668, 670, 672 [M]$^+$; 629, 631, 633, 635, 637 [M − Cl]$^+$; 332, 334, 336 [M/2]$^+$.

(1*S,4*S**,7*S**,8*R**,9*S**)-1,2,3,4,5,6,9-Heptachloro-9-diethylaminocarbonyltricyclo[6.1.0.0^{4,8}]nona-2,5-dien-7-ol (6).** A solution of compound **2** (0.28 g, 0.60 mmol) in THF (5 mL) was added dropwise to a stirred suspension of $LiAlH_4$ (0.23 g, 6.02 mmol) in anhydrous THF (5 mL). The reaction mixture was stirred at ~20 °C for 1 h. The course of the reaction was monitored by TLC. An excess of $LiAlH_4$ was quenched with water, THF was evaporated, and the residue was extracted with $CHCl_3$ (3×30 mL). The combined organic extracts were dried with $MgSO_4$ and concentrated. The residue was purified by chromatography on a silica gel column (AcOEt—petroleum ether, 1 : 1, as the eluent), and compound **6** was obtained as white crystals in a yield of 0.16 g (57%), m.p. 193—195 °C. Found (%): C, 35.86; H, 2.80; Cl, 51.86; N, 3.15. $C_{14}H_{12}Cl_7NO_2$. Calculated (%): C, 35.44; H, 2.55; Cl, 52.31; N, 2.95. IR, ν/cm^{-1}: 1606, 1630, 3004, 3418. ^{1}H NMR (acetone-d_6), δ: 1.04 and 1.31 (both t, 3 H each, Me, J = 7.1 Hz); 3.21 and 3.28 (both dq, 1 H each, NC$\underline{H}_A$H$_B$, ^2J = −14.2 Hz, ^3J = 7.1 Hz); 3.40 and 3.75 (both dq, 1 H each, NCH$_A\underline{H}_B$, ^2J = −14.2 Hz, ^3J = 7.1 Hz); 5.60 (d, 1 H, H(7), J = 8.3 Hz); 5.77 (d, 1 H, OH, J = 8.3 Hz). ^{13}C NMR (acetone-d_6), δ: 11.53, 13.06 (2 Me); 40.15, 45.03 (2 NCH_2); 49.25 (C(8)); 58.44, 59.82 (C(1), C(9)); 74.35 (C(7)); 81.49 (C(4)); 127.81, 138.30 (C(6), C(2)); 129.46, 141.16 (C(5), C(3)); 161.35 (N—C=O).

4,5,6-Trichloro-7-(*N*,*N*-diethylaminomethyl)indan-1-ol (7). A solution of compound **2** (0.3 g, 0.65 mmol) in THF (10 mL) was added dropwise to a suspension of $LiAlH_4$ (0.25 g, 6.58 mmol) in anhydrous THF (20 mL) under argon. The reaction mixture was refluxed for 12 h, cooled, worked up as described above, and purified by silica gel column chromatography (AcOEt—petroleum ether, 1 : 1, as the eluent) and recrystallization (from an AcOEt—petroleum ether mixture, 1 : 10). Compound **7** was obtained as a white powder, m.p. 155—158 °C. The yield was 0.09 g (~45%). IR, ν/cm^{-1}: 736, 772, 970, 1054, 1162, 1450, 1582, 1654, 3352. ^{1}H NMR (acetone-d_6), δ: 1.08 (t, 6 H, 2 Me, J = 7.2 Hz); 2.44 (m, 4 H, NCH_2, C(3)H$_2$); 2.70 (dq, 2 H, NCH_2, ^2J = −14.4 Hz, ^3J = 7.2 Hz); 2.96 and 3.12 (both m, 1 H each, C(2)H$_2$); 3.87 and 4.06 (both d, 1 H each, CH_2N, J = 13.0 Hz); 5.36 (dd, 1 H, OCH, J = 1.8 Hz, J = 7.3 Hz); 6.38 (br.s, 1 H, OH). ^{13}C NMR, δ: 10.64 (Me); 31.04 (C(3)); 31.81 (C(2)); 45.95, 52.87 (NCH_2); 75.06 (C(1)); 129.11, 129.73, 131.81, 133.68 (C(5), C(4), C(6), C(3a)); 142.58 (C(7)); 147.91 (C(7a)).

4,5-Dichloro-7-diethylaminocarbonylindan-1-one (8). An activated Zn powder (0.28 g, 4.30 mmol) was added portionwise to a solution of compound **2** (0.2 g, 0.43 mmol) in an acetone—THF mixture (1 : 1, v/v, 10 mL) containing glacial acetic acid (1 mL). The reaction mixture was stirred for 1 h and then filtered. The filtrate was concentrated *in vacuo*, the residue was dissolved in AcOEt, and the solution was washed with a saturated NaCl solution. The organic layer was dried with $MgSO_4$

and filtered. The solvent was evaporated and the residue was chromatographed on a silica gel column (AcOEt—petroleum ether, 1 : 1, as the eluent). Compound **8** was obtained as colorless crystals in a yield of 0.1 g (77%), m.p. 138—140 °C. Found (%): C, 56.40; H, 4.86; Cl, 23.33; N, 4.86. $C_{14}H_{15}Cl_2NO_2$. Calculated (%): C, 56.02; H, 5.04; Cl, 23.62; N, 4.67. IR, ν/cm^{-1}: 712, 790, 1066, 1120, 1192, 1588, 1642, 1714. ^{1}H NMR ($CDCl_3$), δ: 1.02 and 1.31 (both t, 3 H each, Me, J = 7.2 Hz); 2.72 (dd, 2 H, C(3)H_2, ^3J = 6.9 Hz, ^3J = 3.3 Hz); 3.06 (m, 4 H, C(2)H_2, CH_2N); 3.62 (q, 2 H, CH_2N, ^2J = 14.2 Hz, ^3J = 7.2 Hz); 7.60 (s, 1 H, =CH). ^{13}C NMR ($CDCl_3$), δ: 12.09, 13.48 (Me); 24.43 (C(3)); 36.01 (C(2)); 38.78, 42.51 (NCH_2); 130.81, 131.99, 133.15, 135.89 (C(7), C(4), C(3a), C(5)); 134.27 (C(6)); 151.55 (C(7a)); 163.91 (N—C=O); 202.78 (C=O). MS, m/z: 299, 301 $[M]^+$; 264, 266 $[M - Cl]^+$; 227, 229 $[M - NEt_2]^+$; 72 $[NEt_2]^+$.

We thank the referee for valuable advice and discussion of the possible mechanisms of the reactions in question.

This study was financially supported by the Russian Foundation for Basic Research (Project No. 02-03-32594a).

References

1. J. S. Newcomer and E. T. McBee, *J. Am. Chem. Soc.*, 1949, **71**, 946.
2. E. D. Weil and J. Linder, *J. Org. Chem.*, 1963, **28**, 2218.
3. P. E. Eaton, D. Tang, and R. Gilardi, *Tetrahedron Lett.*, 2002, **43**, 3.
4. F. A. Gimalova, O. A. Gavrilov, D. V. Lyubetskii, and M. S. Miftakhov, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 2157 [*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 2278]; F. A. Gimalova, O. A. Gavrilov, D. G. Golovanov, V. K. Mavrodiev, and M. S. Miftakhov, *Mendeleev Commun.*, 2003, **13**, 232.
5. R. R. Akhmetvaleev, L. R. Imaeva, and M. S. Miftakhov, *Zh. Org. Khim.*, 1997, **33**, 1342 [*Russ. J. Org. Chem.*, 1997, **33** (Engl. Transl.)].
6. G. Mehta and S. S. Ramesh, *Chem. Commun.*, 2000, 2429; D. S. Reddy, G. Mehta, S. S. Ramesh, and U. Tatu, *Tetrahedron Lett.*, 1999, **40**, 9141.
7. G. A. Grob, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 535; P. Weyerstahl and H. Marshall, in *Comprehensive Organic Synthesis*, Eds B. M. Trost, I. Fleming, and E. Winterfeldt, Pergamon Press, Oxford, 1991, **6**, 1044.
8. M. I. Rybinskaya, A. N. Nesmeyanov, and N. K. Kochetkov, *Usp. Khim.*, 1969, **38**, 961; 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.)].
9. G. Rosenkranz, O. Mancera, J. Gatica, and C. Djerassi, *J. Am. Chem. Soc.*, 1950, **72**, 4077.
10. J. R. Hanson and E. Premusic, *Angew. Chem., Int. Ed. Engl.*, 1968, **7**, 247; C. R. Johnson, J. E. Keiser, and J. C. Sharp, *J. Org. Chem.*, 1969, **34**, 860.
11. J. R. Hanson, *Synthesis*, 1974, 1; N. A. Saccomano, in *Comprehensive Organic Synthesis*, Eds B. M. Trost, I. Fleming, and S. L. Schreiber, Pergamon Press, Oxford, 1991, **1**, 173.
12. L. C. Pauling, *The Nature of the Chemical Bond*, 2nd ed., Cornell Univ. Press, USA, 1940, 58.
13. I. A. Gaisina, N. K. Selezneva, O. V. Tikhonov, L. V. Spirikhin, and M. S. Miftakhov, *Izv. Akad. Nauk,* 1997, 1900 [*Russ. Chem. Bull.*, 1997, **46**, 1804 (Engl. Transl.)].
14. J. Wiemann, P.-F. Casals, and S. Risse, *Bull. Soc. Chim. Fr.*, 1963, 1281.
15. P. Cintas, *Synthesis*, 1992, 248; M. Avalos, R. Babiano, P. Cintas, J. L. Jimenez, and J. C. Palacios, *Chem. Soc. Rev.*, 1999, **28**, 169.
16. J. A. Dodge, J. I. Trujillo, and M. Presnell, *J. Org. Chem.*, 1994, **59**, 234.
17. J. K. Whitesell and D. E. Allen, *J. Am. Chem. Soc.*, 1988, **110**, 3585.
18. R. M. Scarborough, B. H. Toder, and A. B. Smith, III, *J. Am. Chem. Soc.*, 1980, **102**, 3904.
19. R. Mori and M. Tsuji, *Tetrahedron*, 1988, **44**, 2835.

Received July 24, 2003;
in revised form April 14, 2006