On the mechanism of the $Fe(CO)_5$-catalyzed Kharasch reaction

1. Stereochemistry of addition of $BrCCl_3$ to (*R*)-3-(*E*)-cinnamoyl-4-phenyloxazolidin-2-one, (*R*)-3-(*E*)-acryloyl-4-phenyloxazolidin-2-one, and their π-complexes with $Fe(CO)_4$

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Regioselectivity and diastereoselectivity of the addition of $BrCCl_3$ to (*R*)-3-(*E*)-cinnamoyl-4-phenyloxazolidin-2-one (**1**) and (*R*)-3-(*E*)-acryloyl-4-phenyloxazolidin-2-one (**2**) catalyzed by $Fe(CO)_5$ or initiated with benzoyl peroxide were investigated. Stereochemistry of the reaction of $BrCCl_3$ with the π-complexes (4*R*,α*S*,β*S*)-η²-(3-(*E*)-cinnamoyl-4-phenyloxazolidin-2-one)irontetracarbonyl (**3a**) and (4*R*,α*R*)-η²-(3-acryloyl-4-phenyloxazolidin-2-one)irontetracarbonyl (**4b**) was also studied. The results obtained allow the following conclusions to be drawn: (1) the thermal Kharasch reaction catalyzed by $Fe(CO)_5$ proceeds by a redox catalysis mechanism; (2) iron (in any of its oxidation states) is not coordinated to olefins in the transition state of the reaction; (3) the transfer of the halogen atom on the radical adduct probably occurs inside a radical—iron cation pair.

Key words: Kharasch reaction, regioselectivity, diastereoselectivity, catalysis, iron pentacarbonyl, bromotrichloromethane, addition, olefins, π-complexes, mechanism, redox catalysis.

The addition of haloalkanes to olefins catalyzed by low-valence transition metal complexes (TMC) is a well-known method for the formation of a C—C bond.[1,2] The Kharasch reaction,[3] *i.e.*, the addition of polyhaloalkanes to olefins, belongs to the same type and is undoubtedly a significant reaction from the synthetic viewpoint. The mechanism of the catalysis of the Kharasch reaction by TMC is still debated. However, knowing the mechanism is a key factor for the development of an efficient catalytic asymmetric synthesis of adducts that can be used as synthons for the preparation of a wide number of optically active organic compounds.

At various stages of investigation of the thermal TMC-catalyzed Kharasch reaction, the mechanisms illustrated in Scheme 1 have been suggested for it (the ligand environment of the metal is not shown for the sake of simplicity):

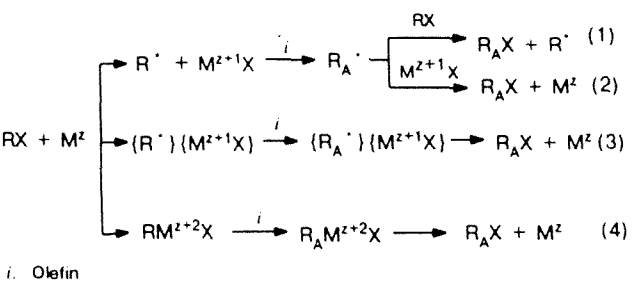
(1) a purely radical mechanism according to which the function of the TMC is only the generation of radical R˙ from RX with the chain transfer *via* the abstraction of the halogen atom from RX by the adduct radical $R^{\cdot}_{A}$ resulting from the addition of R˙ to the olefin;[4]

(2) a redox-catalytic mechanism, which differs from the previous one in that the chain transfer is accomplished by the transfer of halogen from MX to the adduct radical;[4,5]

(3) a modified redox-catalytic mechanism in which it is stated that both the initial radical R˙ and the adduct radical $R^{\cdot}_{A}$ form radical-cation pairs with the metal ion, and the transfer of the halogen atom to $R^{\cdot}_{A}$ occurs inside these pairs.

(4) a metal-complex mechanism that involves oxidative addition of RX to complex M to give the RMX species followed by the insertion of olefin into the R—M bond and reductive elimination of the addition product with regeneration of the catalytic complex.[7,8]

Scheme 1



i. Olefin

The redox-catalysis mechanism (2) is now the generally accepted mechanism for the TMC catalysis of the Kharash reaction.[1] However, the simple redox catalysis cannot account for the asymmetric induction in the reactions catalyzed by chiral complexes of Ru^{II} [9] and

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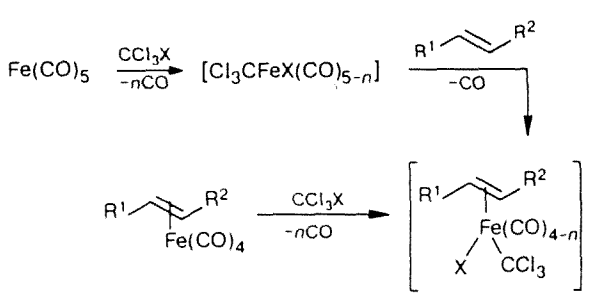
Rh^I.[10] For this purpose, mechanisms (3) and (4) may be invoked. Additional evidence for the participation of the metal in the transition state of the process is provided by the difference in the ρ values found for the Cu^I- and Ru^{II}-catalyzed addition of $BrCCl_3$ to substituted styrenes.[11] The isolation of the relatively stable product of oxidative addition of CCl_4 to the Rh^I [12] makes metal-complex mechanism (4) more probable, at least, for catalysts based on Rh^I и Ru^{II}.

The principal mechanism of the catalysis of the Kharasch reaction by mononuclear TMC, involving the formation of carbon-centered radicals (mechanisms (1)—(3)) or not involving their formation (mechanism (4)), is apparently determined, most of all, by the nature of the metal in the catalytic complex. The variation of the charge of the TMC in the catalytic cycle shown in Scheme 1 implies that for complexes of the transition metals that act as one-electron reducing agents (for example, complexes of Cu^I or Fe^{II}), a pathway involving the formation of carbon-centered radicals ((1)—(3)) is the most likely. For TMC acting as two-electron reducing agents (for example, Rh^I or Ru^{II}), metal-complex mechanism (4) is probably preferred. In the case of TMC capable of acting as both one-electron and two-electron reducing agents, the reaction may occur by a mixed mechanism.

$Fe(CO)_5$ is one of the most widely used catalysts of the Kharash reaction.[2,13] It has been assumed that during this reaction, Fe^0 is oxidized to Fe^I, which is an extremely unstable oxidation state of Fe.[14] Since +2 is one of the most stable oxidation states of Fe, the two-electron oxidation of Fe^0 to Fe^{II} would be more favorable. Therefore, for the Kharasch reaction catalyzed by $Fe(CO)_5$, metal-complex mechanism (4) cannot be ruled out *a priori*. In 1982, this mechanism was suggested for the addition of polyhalomethanes to trialkylvinylsilanes catalyzed by Fe^0 complexes.[15] However, the data given in Ref. 15 are inadequate for accepting or rejecting this viewpoint. Later, no special studies devoted to this problem have been carried out.

It may be assumed that if the reaction proceeds by the metal-complex catalysis mechanism (4), the addition of polyhaloalkanes to olefins in the presence of $Fe(CO)_5$ and the addition to the olefinic π-complex will involve the same intermediate iron-containing species (Scheme 2).

Scheme 2



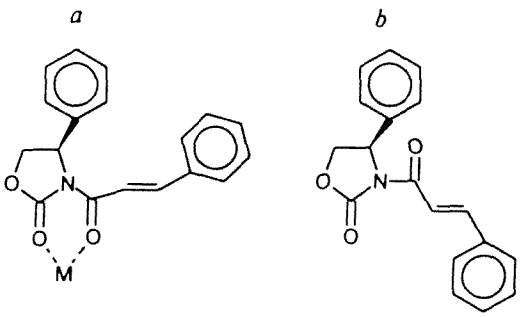


Fig. 1. Conformations of olefin **1** σ-coordinated to the metal ion (*a*) and in the free form (*b*)

We believed that the use of chiral substrates capable of forming both π-complexes with Fe^0 and/or σ-complexes with oxidized forms of iron will be an aid in obtaining reliable data concerning participation of the metal in the transition state of the Kharasch reaction. For this purpose, it is necessary to compare the diastereoselectivity of the addition in the presence of a standard radical initiator and the diastereoselectivity of the $Fe(CO)_5$-catalyzed addition with that of the addition to the π-complexes of Fe^0.

We used (*R*)-3-(*E*)-cynnamoyl-4-phenyloxazolidin-2-one (**1**) and (*R*)-3-acryloyl-4-phenyloxazolidin-2-one (**2**) as chiral substrates.

It has been shown previously that nucleophilic addition of organocopper compounds to the β-carbon atom of compound **1** [16] and the subsequent bromination of the intermediate α-carbanion[17] are highly diastereoselective. This is caused, among other reasons, by the chelate formation between the initial substrate and the metal ion, which results in one of the diastereotopic sides of the double bond being efficiently shielded by the phenyl substituent of the oxazolidinone fragment (Fig. 1, *a*).

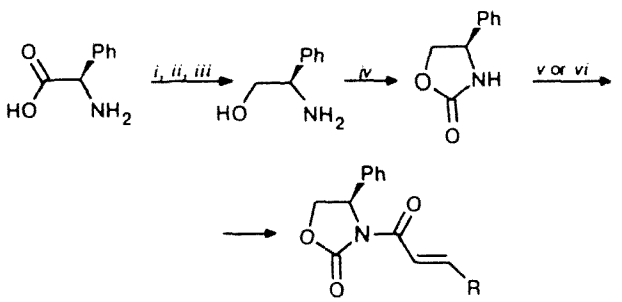
This is confirmed by the fact that in the absence of coordination, reactions in systems of this type occur with low diastereoselectivities.[18] By analogy with the previously reported data,[18] we may assume that molecule **1** exists predominantly as a conformation with the *trans*-arrangement of the carbonyl oxygen atoms (Fig. 1, *b*) in which the reaction center is shielded to only a small extent. According to the data of quantum-mechanical calculations carried out in this work, the energy of this conformation of compound **1** is lower than that of the conformation having the closest energy by 2 kcal mol^{-1}.

In the present work we studied the stereochemistry of the addition of $BrCCl_3$ to olefins **1** and **2** initiated by benzoyl peroxide (BP) or catalyzed by $Fe(CO)_5$. For comparison, we studied the stereochemistry of the addition of $BrCCl_3$ to coordinated olefins in the diastereomerically pure complexes (4*R*,α*S*,β*S*)-[(η^2-**1**)$Fe(CO)_4$] (**3a**) and (4*R*,α*R*)-[(η^2-**2**)$Fe(CO)_4$] (**4b**).

Results and Discussion

The initial compounds **1** and **2** were synthesized according to Scheme 3, starting from (*R*)-2-phenylglycine. This pathway, unlike that suggested previously,[16] included two new steps: esterification of (*R*)-2-phenylglycine and the subsequent reduction of the methyl ester with $LiAlH_4$. We found that this scheme leads to partly racemized (*R*)-4-phenyloxazolidin-2-one. Nevertheless, the optically pure compound can be isolated (in low yield) by crystallization of the crude product. We did not study in detail the reasons for the racemization. It is noteworthy that acylation of (*R*)-4-phenyloxazolidin-2-one with (*E*)-cinnamoyl chloride can be carried out in the presence of Et_3N (in the original procedures,[16,19] BuLi was used as the base). However, acylation with acryloyl chloride in the presence of Et_3N yields mostly a polymer of unknown structure. The use of *t*-BuOK as the base leads to the target product **2**, which was isolated after chromatographic purification in 36 % yield.

Scheme 3

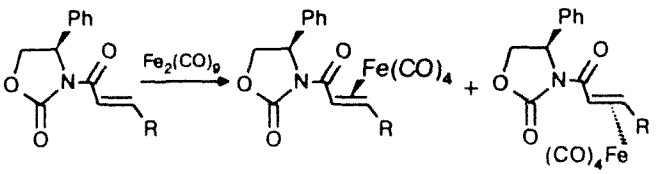


1: R = Ph
2: R = H

Reagents: *i* MeOH, $SOCl_2$; *ii*. NH_3, $CHCl_3$; *iii*. $LiAlH_4$, THF; *iv*. $(MeO)_2CO$, K_2CO_3; *v*. PhCH=CHCOCl, Et_3N; *vi*. CH_2=CHCOCl, Bu^tOK

The π-complexes were synthesized from $Fe_2(CO)_9$ and the corresponding olefins **1** and **2** by a previously reported procedure[20] (Scheme 4). The reaction affords a mixture of diastereomeric complexes **3a** and **3b** (in a 2.5 : 1 ratio) and **4a** and **4b** (in a 1.8 : 1 ratio). The individual diastereomers **3a** and **4b** were isolated by crystallizing the products from an *n*-C_6H_{14}–C_6H_6 mixture. The complexes can also be separated by TLC on SiO_2 (with $CHCl_3$ as the eluent); the mobility of **3b** or **4b** is higher than that of **3a** or **4a**. However, our attempts to isolate preparative amounts of complexes **3b** and **4a** by chromatography failed. This is probably caused by the instability of these compounds under the conditions of chromatography.

Scheme 4



1: R = Ph
2: R = H

3a: R = Ph
4a: R = H

3b: R = Ph
4b: R = H

The structure of complex **3a**, determined by X-ray diffraction analysis, is shown in Fig. 2, which indicates that the olefinic carbon atoms are partly sp^3-hybridized and have the (α*S*,β*S*) configuration. Therefore, these atoms in the other diastereomer **3b** should have the (α*R*,β*R*) configuration.

The signal of the β-hydrogen atom in the ^1H NMR spectrum of compound **3b** is shifted upfield by 0.11 ppm with respect to that in the spectrum of **3a**. This shift may be due to the shielding effect of the Ph substituent in position 4 of the oxazolidine fragment. In view of the partial sp^3-hybridization of the olefinic carbon atoms, the β-H atom in **3b** should be located closer to the Ph group than that in **3a**. The shielding effect of the phenyl group was used to assign the configurations of diastereomers **4a** and **4b**. In the case of **4b**, the signals of the β-H_{trans} and β-H_{cis} protons are shifted upfield by 0.03 and 0.08 ppm with respect to the corresponding signals of **4a**. Therefore, we assigned the (4*R*,α*R*) configuration to compound **4b**, whereas (4*R*,α*S*) was assigned to **4a**.

Complexes **3a** and **4b** in the crystalline state are relatively stable in air at ambient temperature. When benzene solutions of the complexes are heated at 80 °C in an inert atmosphere, the complexes undergo epimerization and simultaneously decompose to give free olefins. Under these conditions, **4b** is more stable than **3a**. Epimerization of **3a** occurs rather rapidly, diastereomer **3b** being detected by TLC in the reaction mixture already within 2 min; its decomposition to compound **1** is almost completed over a period of 1.5 h. In the case of **4b**, the formation of **4a** was observed only within 2 h.

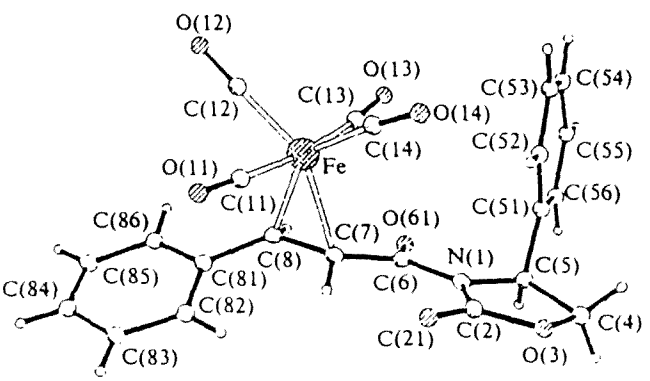
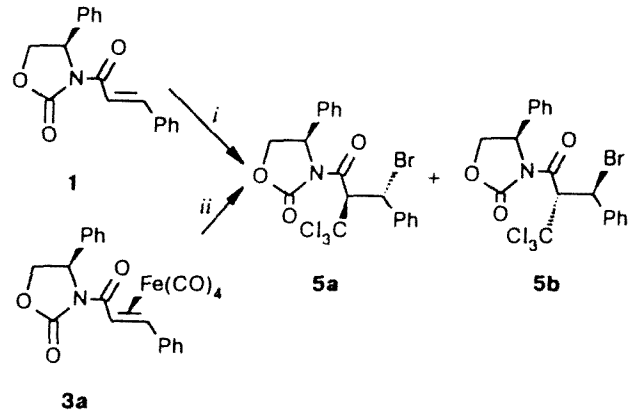


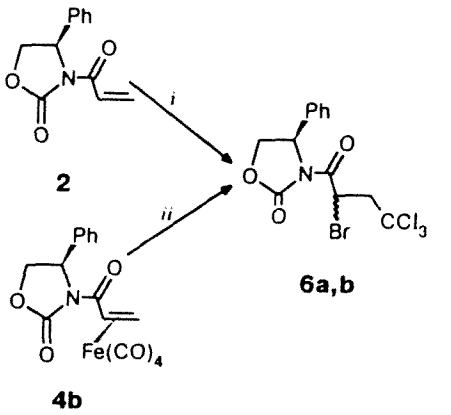
Fig. 2. Structure of molecule **3a**.

Scheme 5



Reagents: *i.* CCl_3Br, $Fe(CO)_5$; *ii.* CCl_3Br

Scheme 6



Reagents: *i.* CCl_3Br, $Fe(CO)_5$; *ii.* CCl_3Br

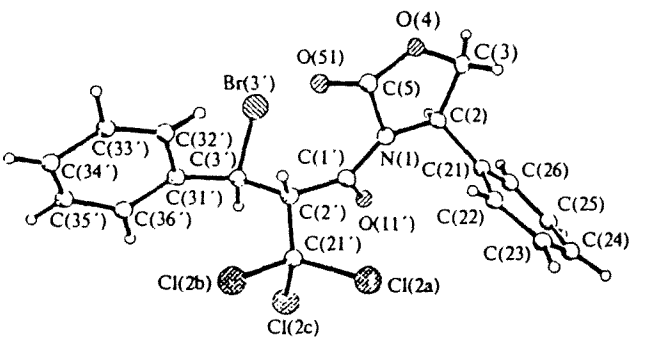


Fig. 3. Structure of molecule **5a**.

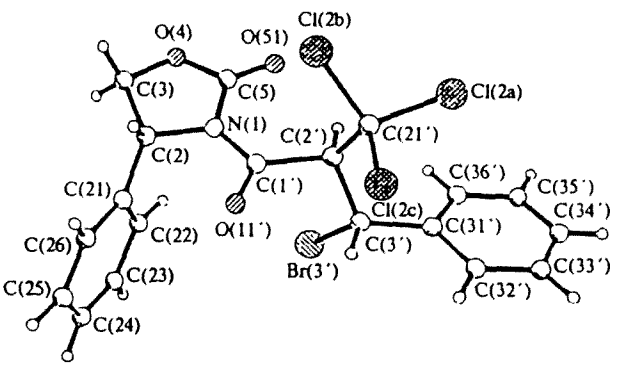


Fig. 4. Structure of molecule **5b**.

and decomposition to olefin **2** did not come to an end in 3 h.

The addition of $BrCCl_3$ to olefins **1** and **2** in the presence of catalytic amounts of $Fe(CO)_5$ was carried out in benzene in sealed tubes under Ar at 80 °C. The reactions with stoichiometric amounts of $Fe(CO)_5$ and with complexes **3a** and **4b** were carried out at 80 °C in an Ar flow in an open setup (Schemes 5 and 6, Table 1).

The absolute configurations and the structures of adducts **5a** and **5b** were determined by X-ray diffraction analysis, and their structures are presented in Figs. 3 and 4, which indicate that compounds **5a** and **5b** are the products of the formal *trans*-addition of $BrCCl_3$ with *anti*-arranged Br and CCl_3 and that their absolute configurations are $4R,\alpha R,\beta S$ and $4R,\alpha S,\beta R$, respectively.

We were not able to isolate adducts **6a** and **6b** in the crystalline state, and their absolute configurations were not determined. The structures of **6a,b** were confirmed by their ^1H NMR spectra. The signals of α-H are exhibited in the 6.1—6.3 ppm region. The signals of α-H for the alternative diastereomers of (4*R*)-3-(β-bromo-α-trichloromethylacetyl)-4-phenyloxazolidin-2-one, by analogy with **5a,b**, should have been located in a higher field (5.4—5.6 ppm).

The data of Table 1 indicate that the peroxide initiation is efficient in the addition of $BrCCl_3$ to olefin **1**; this reaction gave adducts **5** in 28 % yield (run 1). In the case of olefin **2**, a polymer of unknown structure was formed as the major reaction product, whereas virtually no addition products **6** were obtained even when $BrCCl_3$ was used as the solvent (run 10).

There are principal distinctions between the regioselectivities of the addition of $BrCCl_3$ to olefins **1** and **2** (runs 1—7 and 11—13). In fact, in the case of **1**, the CCl_3 group adds to the α-carbon atom of the cinnamoyl fragment, whereas in the case of **2**, it adds to the β-carbon atom of the acryloyl fragment. In the former case, no difference between the regioselectivities of the reactions initiated by peroxide and catalyzed by $Fe(CO)_5$ was observed (runs 1 and 2—5). In both cases, the regioselectivity does not depend on the concentration of $Fe(CO)_5$ (runs 2—7 and 11—13).

When the $Fe(CO)_5$—DMF (1 : 3) system was used[21] as the catalyst, diastereomeric mixtures of the addition products **5** and **6** were isolated from the reaction mixtures in 33 and 17 % yields, respectively (runs 4 and 11). The starting olefin **1** was isolated from the reaction mixture in a yield of 57 %, while **2** was entirely con-

Table 1. Addition of $BrCCl_3$ to olefins **1** and **2** and their π-complexes **3a** and **4b** at 80 °C in benzene

Run	Substrate (S)	c_S (mol L^{-1})	Catalyst	S:Fe:$BrCCl_3$	Additive[a]	Time/h	Adduct	Yield[b] (%)	Ratio between the diastereomers[c]	Recovered compound S (%)
1	**1**	0.72	(BP)	—	—	30	**5a,b**	28	1.2 : 1	68
2	**1**	0.44	$Fe(CO)_5$	10 : 1 : 20	—	4	**5a,b**	11	1 : 1	74
3	**1**	0.45	$Fe(CO)_5$	10 : 1 : 20	—	4	**5a,b**	[d]	1.2 : 1	—
4	**1**	0.44	$Fe(CO)_5$	10 : 1 : 20	DMF	4	**5a,b**	33	1 : 1	57
5	**1**	0.45	$Fe(CO)_5$	10 : 1 : 20	DMF	4	**5a,b**	[d]	1.2 : 1	—
6	**1**	0.34	$Fe(CO)_5$	1 : 1 : 5	—	0.33		[e]		59
7	**1**	0.34	$Fe(CO)_5$	1 : 1 : 5	DMF	0.33	**5a,b**	58	1.3 : 1	29
8	**3a**	0.22	—	1 : 1 : 5	—	0.25	**5a,b**	12	1.7 : 1	84
9	**3a**	0.19	—	1 : 1 : 5	DMF	0.25	**5a,b**	16	1.3 : 1	74
10	**2**	0.4	(BP)	in $BrCCl_3$	—	3		0	0	—
11	**2**	0.46	$Fe(CO)_5$	10 : 1 : 20	DMF	3	**6a,b**	17 (7.3[f])	1 : 1.3	33
12	**2**	0.46	$Fe(CO)_5$	1 : 1 : 5		0.5	**6a,b**	9	1 : 1.9	—
13	**2**	0.46	$Fe(CO)_5$	1 : 1 : 5	DMF	0.5	**6a,b**	33	1 : 1.7	—
14	**4b**	0.26	—	1 : 1 : 5	DMF	0.6	**6a,b**	34 (41[f])	1 : 1.5	—

[a] The Fe:DMF ratio was 1 : 3 in all cases. [b] The yield is based on the starting substrate. [c] Determined as the average ratio of the heights of the signals of the isomer exhibited in a lower field to the heights of the signals of the isomer exhibited at a higher field in the 6.0—6.5 ppm region, which corresponds to the **5a** : **5b** (4*R*,α*R*,β*S*/4*R*,α*S*,β*R*) and **6a** : **6b** ratios (see Experimental). [d] The yield of the adducts was not determined. [e] The signals in the ^1H NMR spectra of the isolated compounds were considerably broadened, which did not allow identification of the adducts. [f] The yield of the reduction product **7** is given in parentheses.

sumed in the reaction, which gave, along with the adducts, 3-(3,3,3,-trichlorobutyryl)-4-phenyloxazolidin-2-one (**7**) (yield 7 %), resulting from reduction of the intermediate radical adduct, and polymeric products. In the absence of DMF, the yield of the products of addition decreased (runs 2 and 4; 12 and 13).

Of the four theoretically possible diastereomers, the addition of $BrCCl_3$ to **1** gives only two compounds with *anti*-arrangement of CCl_3 and Br in an approximately 1 : 1 ratio. This result does not depend on whether $Fe(CO)_5$ or BP was used or on the concentration of $Fe(CO)_5$ (Table 1, runs 1 and 2—7).

The addition of $BrCCl_3$ to **2** catalyzed by $Fe(CO)_5$ affords a mixture of two diastereomers **6a,b** in which **6b** slightly predominates. The diastereoselectivity does not depend on the concentration of $Fe(CO)_5$ (runs 11—13).

To verify the hypothesis of the occurrence of mechanism (4) (Scheme 1 and 2), we studied the stereochemistry of the addition of $BrCCl_3$ to the double bonds in complexes **3a** and **4b**. In view of the thermal instability of these complexes, the durations of these reactions were no longer than 40 min. It was found by TLC that in the presence of $BrCCl_3$ at 80 °C, the starting complexes completely disappear after 5—10 min. It can be seen from the data of Table 1 (*cf.* runs 7 and 9, 13 and 14) that the stereochemical result of the process almost does not depend on the form (free or coordinated) in which olefins **1** and **2** were introduced in the reaction. The introduction of DMF in the reaction mixtures increases the yields of adducts **5**—**6** (runs 8 and 9), as was also observed in the catalytic version of the reaction (runs 2 and 4). When an equimolar amount of $Fe(CO)_5$ reacts with **1** without DMF, the process yields a complex mixture of products that cannot be identified (run 6).

The addition products **5a,b** are formed in a kinetically controlled process. It was shown in special runs that **5a** is not converted into **5b** in the presence of catalytic amounts of $Fe(CO)_5$ over a period of 4 h at 80 °C. The contribution of the thermodynamic factor to the diastereoselectivity of the formation of compounds **6a,b** is probably also small, because in the case of the methyl ester of *N*-(2-bromo-3,3,3-trichloropropionyl)proline, epimerization occurs under these conditions to only a small extent (5—10 %) over a period of 2 h.[22]

The data obtained make it possible to make the following conclusions concerning the mechanism of the addition of $BrCCl_3$ to olefins **1** and **2** catalyzed by $Fe(CO)_5$.

(1) *The metal-complex mechanism (4) is not realized in the reactions studied.* If the reaction proceeded by this mechanism, one could expect, by analogy with the results obtained using Rh^I complexes as catalysts,[12] that the products of the *cis*-addition of $BrCCl_3$ to **1** with the *syn*-arranged Br and CCl_3 fragments and the (4*R*,α*R*,β*R*) and (4*R*,α*S*,β*S*) absolute configurations would be obtained and that the diastereoselectivities of the reactions involving **3a** or **4b** would differ substantially from those of the reactions of noncoordinated ligands. However, this is not the case, and the stereochemical results do not depend on whether the reaction is initiated by BP or catalyzed by $Fe(CO)_5$ (runs 1 and 2—7) or on the form in which the olefin is taken (free or coordinated, runs 2—7 and 8—9, 11—13 and 14).

(2) *The $^{\cdot}CCl_3$ radical is the intermediate reactive species, which adds to the C=C bond of the substrate.* This

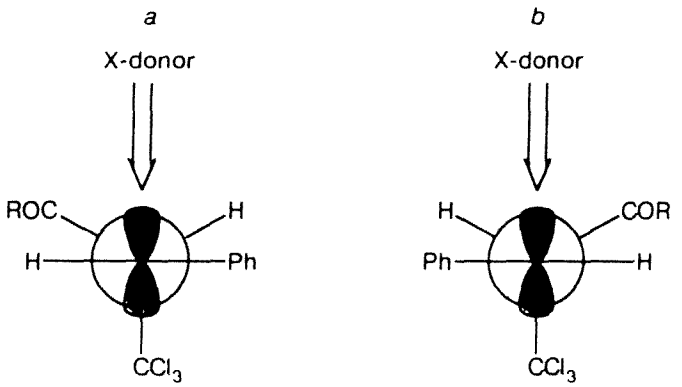


Fig. 5. Schematic representation of the transition state (R = (*R*)-4-phenyloxazolidin-2-on-1-yl) of the transfer of halogen to the adduct radical explaining the formaion of the *anti*-adducts **5a** (*a*) and **5b** (*b*) on the addition of $BrCCl_3$ to olefin **1**.

is indicated by the identical diastereoselectivities and regioselectivities of the addition of $BrCCl_3$ to **1** in the presence of $Fe(CO)_5$ or BP (runs 2—7 and 1). The regioselective addition to compound **1** involving the primary attack on the α-carbon atom, rather than on the β-carbon atom, of the C=C bond can be easily explained by the fact that the intermediate adduct radical formed in this case is more stable, as follows from quantum-mechanical calculations of the energy barriers to the addition of radicals to the C=C bonds.[23] The stability of a radical can be estimated, in its turn, from the energy of the C—X bond, whose cleavage yields this radical.[24] If we take the energies of the C—H bonds in toluene (88 kcal mol^{-1})[24] and ethyl acetate (95 kcal mol^{-1})[25] as a measure of the relative stability of the adduct radicals formed from **1** *via* α- or β-addition, respectively, we obtain that the difference in the stability of these radicals is 8 kcal mol^{-1} in favor of the benzyl radical. Thus, the regiospecificity of the primary attack on the α-carbon atom of **1** is completely explained by the radical nature of the intermediate species of this reaction. The unusually high diastereoselectivity of the formation of *anti*-adducts **5a**,**b** in the addition of $BrCCl_3$ to **1** can also be easily explained by the fact that the attack at the intermediate radical adduct in its most favorable conformation from the side of the CCl_3 radical is sterically hindered (Fig. 5), by analogy with other diastereoselective radical reactions.[26]

(3) *Participation of oxidized iron forms in the σ-type coordination of the ligand in the intermediate state of the reaction is excluded.* In the case of the type of coordination shown in Fig. 1, *a*, one should expect that the diastereoselectivity of the addition would depend on the concentration of $Fe(CO)_5$. However, this was observed neither for olefin **1** nor for olefin **2** (runs 2—5 and 7; 11 and 12—13). Finally, the considerable amount of the reduction product **7** formed from **2** (runs 11 and 14) cannot be due to the reduction of the radical adduct with low-valence iron complexes to the enolate anion coordinated with the Fe ion. This is indicated by the absence of deuterium in compound **7** obtained after decomposition of the reaction mixture by a solution of EDTA in D_2O.

(4) *The type* **3** *or* **4** *π-complexes are not kinetically independent species in the reaction.* First, an examination of Fig. 2 indicates that one of the two diastereotopic sides of the C=C bond in molecule **3a** is completely sterically shielded, and if the complex reacted as an independent species, then, at least, the attack of the radical on the C=C bond of **3a** would be highly diastereoselective. Actually, this is not observed (runs 8 and 9, *cf.* runs 1—5, 7). Second, during the thermal interaction of **1** or **2** with an equivalent amount of $Fe(CO)_5$, no **3** or **4** is detected in the reaction mixture (TLC).

However, one of the characteristic features of the $Fe(CO)_5$-catalyzed addition of $BrCCl_3$ to **2** cannot be explained in the context of the simple radical mechanism of addition. Whereas the BP-initiated addition yields only a polymeric product (run 10), adducts **6** are obtained in the presence of $Fe(CO)_5$ as the catalyst (run 11). At first glance this can be easily explained by the fact that the radical adduct abstracts the Br atom from the bromine-containing iron complex more rapidly than from the initial telogen; therefore, in the presence of [FeBr] complexes, chain transfer can successfully compete with the chain growth, which is not observed for peroxide initiation. However, a thorough analysis of this scheme reveals some inconsistencies. The average energy of the Fe—Br bond (59±23 kcal mol^{-1})[27] is close to the energy of the Br—CCl_3 bond (55.7±1 kcal mol^{-1}),[27] and taking into account the fact that the concentration of the catalytic iron-containing species in the solution is much smaller (at least, by an order of magnitude) than that of the telogen, it is incomprehensible why the transfer of the halogen from [FeBr] is more efficient than that from telogen.

To explain this, we may assume that the reaction occurs by the modified redox catalysis mechanism (3). During this reaction Fe^0 is oxidized with $BrCCl_3$, and the produced $^{\cdot}CCl_3$ radical and then the radical adduct form radical-cation pairs with oxidized forms of iron ("radicaloid species"[9]). The radical adduct, in its turn, abstracts bromine from [FeBr] without leaving its radical-cation pair. Thus, due to purely statistical reasons, the transfer of bromine to the radical adduct inside a radical pair is more likely than the chain growth.

Experimental

All the reagents were at least of the "chemically pure grade". $Fe(CO)_5$ was used without additional purification. Benzene was distilled over P_2O_5 under Ar. DMF was kept over NaOH and distilled under Ar. Ether was dried with Na, and THF was distilled over Ph_2CO—Na. TLC was carried out on

plates with SiO_2 (Merck 60 F254). Column chromatography was performed using Silica gel 60 (Merck). The melting points were not corrected. ^1H NMR spectra were recorded on a Bruker WP-200 instrument; the chemical shifts (in ppm) were referred to an internal standard (HMDS), and the spin-spin coupling constants (J) are given in Hz. The angles of rotation were measured on a Perkin Elmer M241 polarimeter.

(*R*)-4-Phenyloxazolidin-2-one. Thionyl chloride (36 mL, 59.5 g, 0.5 mol) was slowly added dropwise to a stirred mixture of (*R*)-2-phenylglycine (50 g, 0.33 mol) and 150 mL of MeOH. After the addition of the whole quantity of $SOCl_2$, the mixture was boiled with stirring for 4 h and allowed to stand for 12 h at 20 °C. The precipitate was filtered off and washed with dry ether. An additional amount of the product was isolated from the mother liquor by evaporating it to dryness and washing the residue with ether. Both portions were combined and dried in air to a constant weight to give 60 g (90.2 %) of hydrochloride of (*R*)-2-phenylglycine methyl ester, which was placed in 500 mL of $CHCl_3$, and a flow of dry ammonia was passed through this mixture for 3 h with stirring. The precipitated NH_4Cl was filtered off and washed with $CHCl_3$. The mother liquor was concentrated, and the residue was distilled *in vacuo* to give 39.3 g (72.2 %) of methyl ester of (*R*)-2-phenylglycine, b.p. 88—92 °C (3 Torr). The latter was dissolved in 70 mL of THF, and the solution was slowly added dropwise with stirring to a cooled (0 °C) mixture of 100 mL of THF and $LiAlH_4$ (13.5 g, 0.36 mol). The resulting mixture was boiled with stirring for 4 h. After cooling, the reaction mixture was decomposed by the slow addition of 26 mL of a 8% aqueous solution of KOH. The precipitate was filtered off and washed with benzene. The combined organic extracts were evaporated to dryness, the residue was dissolved in benzene, and the solution was dried with Na_2CO_3. Evaporation of the solvent gave 28 g (85.7 %) of partly racemized (*R*)-2-amino-2-phenylethanol, which was used without further purification.

A mixture of 2-amino-2-phenylethanol prepared above (27 g, 0.2 mol), $(MeO)_2CO$ (33 mL, 35.4 g, 0.39 mol), and K_2CO_3 (2.72 g, 0.02 mol) was boiled with stirring for 2.5 h. The reaction mixture was concentrated, and the residue was washed with water and recrystallized from EtOH to give 14.4 g of the product, m.p. 132—134 °C и $[\alpha]_D^{25}$ −14.7 (*c* 2, $CHCl_3$). Concentration of the mother liquor and crystallization of the residue from AcOEt gave 1.5 g (4.6 %) of (*R*)-4-phenyloxazolidin-2-one, m.p. 130—131 °C and $[\alpha]_D^{25}$ −55 (*c* 1, $CHCl_3$) [*cf.* Refs..: for the (*S*)-isomer, m.p. 128—130 °C,[16] 131—132 °C[28]; $[\alpha]_D^{22}$ +58 (*c* 1, $CHCl_3$)[16], +49.5 (*c* 2.1, $CHCl_3$)[29]]. Found (%): C, 66.18; H, 5.56; N, 8.50. $C_9H_9NO_2$. Calculated (%): C, 66.24; H, 5.56; N, 8.58.

(*R*)-3-(*E*)-Cinnamoyl-4-phenyloxazolidin-2-one (1). Triethylamine (2.3 mL, 0.166 mol) was added dropwise with stirring and cooling (0 °C) to a mixture of (*R*)-4-phenyloxazolidin-2-one (2.25 g, 0.138 mol) and (*E*)-PhCH=CHCOCl (2.53 g, 0.152 mol) in 15 mL of anhydrous MeCN. After addition of the whole quantity of Et_3N, cooling was terminated, and stirring was continued for 30 min. The reaction mixture was diluted with water, and the precipitate was filtered off and washed with water. The product was dried in air and recrystallized from ethanol to give 2.8 g (70 %) of compound **1**, m.p. 170—171 °C, $[\alpha]_D^{25}$ −4.1 (*c* 1, $CHCl_3$) [the published data[16] for the (*S*)-isomer: m.p. 169—171 °C], $[\alpha]_D^{25}$ +3.4 (*c* 0.74, $CHCl_3$)]. Found (%): C, 73.76; H, 5.22; N, 4.94. $C_{18}H_{15}NO_3$. Calculated (%): C, 73.70; H, 5.16; N, 4.78. ^1H NMR ($CDCl_3$), δ: 4.27 (dd, 1 H, H′-5, J = 3.8 Hz and 8.6 Hz); 4.69 (dd, 1 H, H″-5, J = 8.6 Hz and 8.6 Hz); 5.53 (dd, 1 H, H-4, J = 3.8 Hz and 8.6 Hz); 7.25—7.45 (m, 8 H, ArH); 7.52—7.60 (m, 2 H, ArH); 7.76 (d, 1 H, α-H, J = 15.7 Hz); 7.94 (d, 1 H, β-H, J = 15.7 Hz).

(*R*)-3-Acryloyl-4-phenyloxazolidin-2-one (2). Potassium *tert*-butoxide (0.74 g, 6.7 mmol) was added to a mixture of (*R*)-4-phenyloxazolidin-2-one (1 g, 6.1 mmol) and 8 mL of anhydrous MeCN cooled to −70 °C, and then CH_2=CHCOCl (0.55 mL, 0.61 g, 6.7 mmol) was slowly added dropwise. The reaction mixture was stirred with cooling for an additional 30 min, then cooling was terminated, and stirring was continued for an additional 1.5 h. After that, the mixture was neutralized with dilute AcOH and extracted with $CHCl_3$. The organic layer was washed successively with an aqueous solution of $NaHCO_3$ and water, dried with $MgSO_4$, and evaporated to dryness. The residue was chromatographed on a column (105×16 mm) with SiO_2 (using $CHCl_3$ as the eluent). The fractions containing the product were combined and concentrated to give an oil, which crystallized after trituration under a layer of hexane at 0 °C. The crystals were filtered off, washed with hexane, and dried in air to give 0.48 g (36 %) of **2**, m.p. 79—82 °C. $[\alpha]_D^{25}$ −38.2 (*c* 1.8, $CHCl_3$). Found (%): C, 66.05; H, 4.99; N, 6.40. $C_{12}H_{11}NO_3$. Calculated (%): C, 66.35; H, 5.10; N, 6.45. ^1H NMR ($CDCl_3$), δ: 4.28 (dd, 1 H, H′-5, J = 3.8 Hz and 8.7 Hz); 4.70 (dd, 1 H, H″-5, J = 8.7 Hz and 8.7 Hz); 5.48 (dd, 1 H, H-4, J = 3.8 Hz and 8.7 Hz); 5.87 (dd, 1 H, β-H_{trans}, J = 2.1 Hz and 10.6 Hz); 6.47 (dd, 1 H, β-H_{cis}, J = 2.1 Hz and 16.9 Hz); 7.22—7.45 (m, 5 H, ArH); 7.51 (dd, 1 H, α-H, J = 10.6 Hz and 16.9 Hz).

(4*R*,α*S*,β*S*)-η²-(3-(*E*)-Cinnamoyl-4-phenyloxazolidin-2-one)irontetracarbonyl (3a) and (4*R*,α*R*)-η²-(3-acryloyl-4-phenyloxazolidin-2-one)irontetracarbonyl (4b). Mixtures of diastereomers **3a**+**3b** and **4a**+**4b** were synthesized by a known procedure.[20] To remove traces of oxidized iron, a benzene solution of the diastereomers was passed through a not very thick layer of silica gel. The solvent was evaporated, the residue was dissolved in the minimum amount of benzene at 40 °C, hexane was added until the solution became slightly turbid, and the product was allowed to crystallize at 0 °C. Individual diastereomers **3a** and **4b** were isolated.

3a, yield 38 %, m.p. 126—127 °C, $[\alpha]_D^{25}$ +274.8 (*c* 0.12, C_6H_6). Found (%): C, 57.44; H, 3.26; N, 2.94. $C_{22}H_{15}FeNO_7$. Calculated (%): C, 57.29; H, 3.28; N, 3.04. ^1H NMR (C_6D_6), δ: 3.49 (dd, 1 H, H′-5, J = 3.4 Hz and 8.2 Hz); 3.58 (dd, 1 H, H″-5, J = 8.2 Hz and 8.2 Hz); 4.74 (dd, 1 H, H-4, J = 3.4 Hz and 8.2 Hz); 5.16 (d, 1 H, α-H, J = 10.4 Hz); 5.71 (d, 1 H, β-H, J = 10.4 Hz); 6.7—7.3 (m, 10 H, ArH).

4b, yield 17 %, m.p. 130—132 °C, $[\alpha]_D^{25}$ −301.7 (*c* 0.12, C_6H_6). Found (%): C, 50.63; H, 2.83; N, 3.39. $C_{16}H_{11}FeNO_7$. Calculated (%): C, 49.90; H, 2.88; N, 3.64. ^1H NMR (C_6D_6), δ: 1.98 (d, 1 H, β-H_{trans}, J = 7.3 Hz); 2.66 (d, 1 H, β-H_{cis}, J = 11.5 Hz); 3.32 (dd, 1 H, H′-5, J = 4.2 Hz and 8.4 Hz); 3.52 (dd, 1 H, H″-5, J = 8.4 Hz and 8.4 Hz); 4.32 (dd, 1 H, α-H, J = 7.3 Hz and 11.5 Hz); 4.73 (dd, 1 H, 4-H, J = 4.2 Hz and 8.4 Hz); 6.90 (s, 5 H, ArH).

The addition of $BrCCl_3$ to compounds 1, 2, 3a, and 4b was carried out at 80 °C. All the reactions were carried out in an open system in a slow flow of Ar, except for the reactions in which $Fe(CO)_5$ was taken in catalytic amounts. In these cases, sealed tubes were used, and traces of air were removed from these tubes by the freezing—evacuation—filling with Ar—thawing cycle repeated twice. The reaction conditions are presented in Table 1. When $Fe(CO)_5$ was used, the reaction mixtures were diluted with $CHCl_3$, washed with water, dried with $MgSO_4$, and concentrated. The mixtures were fractionated by preparative TLC on SiO_2 (n-C_6H_{14}—Et_2O—C_6H_6, 1 : 1 : 4) using authentic samples. The R_f value of adduct **5a** is greater than that of **5b**. Individual diastereomers **5a** and **5b** were

Table 2. Crystallographic parameters of **3a**, **5a**, and **5b**, parameters of X-ray diffraction experiments, and final residual factors

Parameter	**3a**	**5a**	**5b**
T/K	160	293	293
Molecular formula	$C_{22}H_{15}FeNO_7$	$C_{19}H_{15}BrCl_3NO_3$	$C_{19}H_{15}BrCl_3NO_3 \cdot 1/3C_6H_6$
Molecular weight	461.2	491.6	517.6
Symmetry	Monoclinic	Monoclinic	Rhombohedral
Space group	$P2_1$	$P2_1$	$R3$
a/Å	11.339(8)	11.304(10)	25.316(6)
b/Å	6.969(4)	6.571(5)	
c/Å	13.0087(8)	14.110(12)	9.159(3)
β/deg	97.50(2)	101.46(2)	
V/Å^3	1025(1)	1027(14)	5084(3)
Z	2	2	9
The number of measured reflexes	5025	5544	3383
The number of reflexes with $I > 6\sigma(I)$	1090	1728	2120
R	0.0472	0.0653	0.0717
R_w	0.0479	0.0753	0.0669

isolated by preparative TLC followed by crystallization from a benzene—hexane mixture. Diastereomers **6a** and **6b** and the reduction product **7** were characterized by ^{1}H NMR spectroscopy. Since very small amounts of compounds **5b**, **6a,b**, and **7** were obtained, the elemental analysis of these compounds was not carried out. Diastereomeric compositions of the addition products were determined by ^{1}H NMR using the heights of peaks at 6—6.5 ppm. The results obtained are presented in Table 1.

(4*R*,α*R*,β*S*)-3-(β-Bromo-β-phenyl-α-trichloromethylpropionyl)-4-phenyloxazolidin-2-one (5a), m.p. 154—155 °C (hexane—C_6H_6), $[\alpha]_D^{25}$ −122.4 (*c* 1.9, C_6H_6). Found (%): C, 46.47; H, 3.04; N, 2.65. $C_{19}H_{15}BrCl_3NO_3$. Calculated (%): C, 46.42; H, 3.08; N, 2.84. ^{1}H NMR ($CDCl_3$), δ: 4.38 (dd, 1 H, H′-5, J = 3.6 Hz and 8.7 Hz); 4.76 (dd, 1 H, H″-5, J = 8.7 Hz and 8.7 Hz); 5.54 (dd, 1 H, H-4, J = 3.6 Hz and 8.7 Hz); 5.57 (d, 1 H, α-H, J = 10.6 Hz); 6.52 (d, 1 H, β-H, J = 10.6 Hz); 7.21—7.41 (m, 8 H, ArH); 7.48—7.62 (m, 2 H, ArH).

(4*R*,α*S*,β*R*)-3-(β-Bromo-β-phenyl-α-trichloromethylpropionyl)-4-phenyloxazolidin-2-one (5b), m.p. 120—124 °C (hexane—C_6H_6). ^{1}H NMR ($CDCl_3$), δ: 4.38 (dd, 1 H, H′-5, J = 3.7 Hz and 8.7 Hz); 4.73 (dd, 1 H, H″-5, J = 8.7 Hz and 8.7 Hz); 5.47 (d, 1 H, α-H, J = 10.6 Hz); 5.52 (dd, 1 H, H-4, J = 3.7 Hz and 8.7 Hz); 6.51 (d, 1 H, β-H, J = 10.6 Hz); 7.1—8.7 (m, 10 H, ArH).

3-(α-Bromo-β,β,β-trichlorobutyryl)-4-phenyloxazolidin-2-one (6a, the minor diastereomer). ^{1}H NMR ($CDCl_3$), δ: 3.26 (dd, 1 H, β-H′, J = 2.1 Hz and 15.0 Hz); 4.05 (dd, 1 H, β-H″, J = 8.7 Hz and 15.0 Hz); 4.32 (dd, 1 H, H′-5, J = 4.4 Hz and 9.4 Hz); 4.76 (dd, 1 H, H″-5, J = 9.4 Hz and 9.4 Hz); 5.50 (dd, 1 H, H-4, J = 4.4 Hz and 9.4 Hz); 6.22 (dd, 1 H, α-H, J = 2.1 Hz and 8.7 Hz); 7.3—7.5 (m, 5 H, ArH).

3-(α-Bromo-β,β,β-trichlorobutyryl)-4-phenyloxazolidin-2-one (6b, the major diastereomer). ^{1}H NMR ($CDCl_3$), δ: 3.25 (dd, 1 H, β-H′, J = 1.9 Hz and 15.7 Hz); 3.99 (dd,

Table 3. Coordinates of the atoms (×10^4) and equivalent isotropic temperature factors ($U \cdot 10^3$/Å^2) for the structure of **3a**

Atom	*x*	*y*	*z*	*U*
Fe	1255(1)	0	2251(1)	16(1)
O(3)	5391(5)	−645(11)	4963(5)	31(1)
O(11)	−468(6)	344(12)	3758(5)	40(1)
O(12)	−723(6)	912(12)	619(6)	49(1)
O(13)	2702(6)	247(13)	528(5)	38(1)
O(14)	2576(6)	3270(11)	3262(6)	33(1)
O(21)	3420(6)	−846(11)	4959(6)	38(1)
O(61)	3661(6)	−3960(11)	1986(5)	25(1)
N(1)	4324(6)	−1764(11)	3516(6)	14(1)
C(2)	4281(9)	−1060(13)	4505(8)	26(1)
C(4)	6274(9)	−1119(15)	4278(8)	40(1)
C(5)	5542(7)	−1752(13)	3249(7)	15(1)
C(51)	5660(7)	−364(11)	2376(6)	10(1)
C(52)	5196(8)	1476(13)	2345(8)	24(1)
C(53)	5233(9)	2685(14)	1522(9)	37(1)
C(54)	5764(9)	2062(14)	689(8)	34(1)
C(55)	6285(7)	303(15)	706(8)	33(1)
C(56)	6233(8)	−977(15)	1537(7)	33(1)
C(6)	3416(7)	−2402(13)	2792(8)	18(1)
C(7)	2165(8)	−2227(13)	3045(7)	15(1)
C(8)	1234(9)	−2941(13)	2303(9)	23(1)
C(81)	144(8)	−3909(13)	2589(7)	18(1)
C(82)	−71(8)	−4128(13)	3627(8)	27(1)
C(83)	−1128(8)	−4931(16)	3830(7)	27(1)
C(84)	−1966(8)	−5569(12)	3040(8)	24(1)
C(85)	−1748(8)	−5449(13)	2027(8)	32(1)
C(86)	−704(8)	−4528(12)	1821(8)	24(1)
C(11)	212(8)	195(15)	3193(7)	27(1)
C(12)	29(8)	593(13)	1273(7)	24(1)
C(13)	2166(8)	99(15)	1217(8)	29(1)
C(14)	2029(9)	2090(15)	2829(9)	31(1)

Table 4. Coordinates of the atoms ($\times 10^4$) and equivalent isotropic temperature factors ($U \cdot 10^3/Å^2$) for the structure of **5a**

Atom	x	y	z	U
Br(3')	2281(3)	0	1425(2)	52(1)
Cl(2a)	3019(8)	−6801(12)	3764(4)	52(2)
Cl(2b)	5233(9)	−5386(12)	3248(5)	59(2)
Cl(2c)	4044(8)	−2949(12)	4472(4)	48(1)
O(4)	−99(18)	−5713(23)	490(11)	52(2)
O(51)	1940(16)	−5062(22)	662(10)	37(2)
O(11')	1429(16)	−2553(23)	3257(9)	42(2)
N(1)	925(20)	−4578(25)	1940(11)	52(2)
C(2)	−354(22)	−4606(28)	1984(13)	70(2)
C(3)	−1079(21)	−5493(29)	1051(14)	96(2)
C(5)	1026(24)	−5204(27)	885(16)	80(2)
C(21)	−628(22)	−5774(28)	2867(16)	59(2)
C(22)	−74(21)	−7645(27)	3091(12)	44(2)
C(23)	−395(22)	−8863(27)	3830(17)	58(2)
C(24)	−1204(21)	−8031(27)	4385(13)	49(2)
C(25)	−1620(23)	−6082(27)	4206(21)	70(2)
C(26)	−1413(21)	−4983(27)	3478(14)	37(2)
C(1')	1860(21)	−3619(22)	2592(10)	11(2)
C(2')	3138(21)	−3609(22)	2546(11)	13(2)
C(3')	3575(21)	−1512(22)	2325(11)	36(2)
C(21')	3797(20)	−4565(21)	3428(10)	8(2)
C(31')	4715(25)	−1372(23)	1969(11)	113(2)
C(32')	4679(24)	−2387(27)	1045(15)	105(2)
C(33')	5639(22)	−2143(28)	719(15)	75(2)
C(34')	6809(23)	−1291(27)	1109(18)	63(2)
C(35')	6808(26)	−375(25)	1892(23)	154(2)
C(36')	5848(22)	−361(23)	2404(16)	50(2)

Table 5. Coordinates of the atoms ($\times 10^4$) and equivalent isotropic temperature factors ($U \cdot 10^3/Å^2$) for the structure of **5b**

Atom	x	y	z	U
Br(3')	−7620(1)	−1888(1)	0	74(1)
Cl(2a)	−9138(1)	−1118(1)	−230(3)	58(1)
Cl(2b)	−9517(2)	−1760(2)	2464(5)	75(2)
Cl(2c)	−8378(2)	−611(1)	2299(4)	67(1)
O(4)	−9512(4)	−3569(3)	2310(9)	62(4)
O(51)	−9432(3)	−2957(3)	506(9)	60(4)
O(11')	−8166(3)	−1664(3)	3382(9)	56(3)
N(1)	−8832(3)	−2593(3)	2578(9)	36(3)
C(2)	−8770(5)	−2863(5)	3953(12)	44(5)
C(3)	−9289(8)	−3523(6)	3743(18)	69(7)
C(5)	−9287(4)	−3032(4)	1664(12)	44(4)
C(21)	−8153(5)	−2783(4)	4226(12)	51(5)
C(22)	−7872(6)	−2960(7)	3181(18)	72(7)
C(23)	−7284(9)	−2877(9)	3543(29)	100(12)
C(24)	−7003(9)	−2618(8)	4791(24)	95(10)
C(25)	−7278(7)	−2447(7)	5803(23)	95(9)
C(26)	−7839(7)	−2512(7)	5520(19)	75(8)
C(1')	−8500(4)	−1966(4)	2418(11)	36(4)
C(2')	−8552(4)	−1675(3)	1003(10)	32(4)
C(3')	−7914(4)	−1299(4)	374(12)	45(5)
C(21')	−8862(4)	−1302(4)	1351(11)	45(4)
C(31')	−7846(4)	−956(4)	−1017(12)	46(5)
C(32')	−7501(6)	−325(6)	−990(17)	70(6)
C(33')	−7473(8)	14(7)	−2225(21)	91(9)
C(34')	−7766(9)	−284(10)	−3463(22)	107(12)
C(35')	−8085(9)	−901(9)	−3511(25)	89(10)
C(36')	−8117(6)	−1228(7)	−2284(15)	65(7)
C(1S)*	−8(35)	−501(18)	2756(54	230(34)
C(2S)*	−522(14)	−490(16)	2674(36)	156(16)

* Coordinates of two independent atoms of the benzene molecule located on a threefold axis.

1 H, β-H", J = 9.9 Hz and 15.7 Hz); 4.40 (dd, 1 H, H'-5, J = 3.2 Hz and 9.1 Hz); 4.79 (dd, 1 H, H"-5, J = 9.1 Hz and 9.1 Hz); 5.46 (dd, 1 H, H-4, J = 3.2 Hz and 9.1 Hz); 6.13 (dd, 1 H, α-H, J = 1.9 Hz and 9.9 Hz); 7.2—7.5 (m, 5 H, ArH).

(4*R*)-4-Phenyl-3-(β,β,β-Trichlorobutyryl)oxazolidin-2-one (7). ^{1}H NMR ($CDCl_3$), δ: 3.04 (t, 2 H, β-H, J = 7.5 Hz); 3.45 (t, 2 H, α-H, J = 7.5 Hz); 4.33 (dd, 1 H, H'-5, J = 3.1 Hz and 8.5 Hz); 4.73 (dd, 1 H, H"-5, J = 8.5Hz and 8.5 Hz); 5.43 (dd, 1 H, H-4, J = 3.1 Hz and 8.5 Hz); 7.2—7.5 (m, 5 H, ArH).

Quantum-mechanical calculations were carried out in the MNDO/PM3 approximation using the MOPAC program on an IBM-compatible computer with a 486 CPU.

X-ray structural study. Crystals of **3a** suitable for an X-ray structural study were obtained by slow cooling of an ethereal solution saturated at 36 °C; crystals of **5a** and **5b** were obtained in a similar way from solutions in a hexane—benzene mixture saturated at 40 °C. The X-ray structural data were obtained on a Siemens P3/PC diffractometer (λMo-Kα, θ-2θ-scanning). The crystallographic data are presented in Table 2. All the structures were solved by the direct method and refined in the full-matrix anisotropic approximation for nonhydrogen atoms. Hydrogen atoms were identified from differential Fourier synthesis and refined in the isotropic approximation. The coordinates of the atoms are listed in Tables 3—5. All the calculations were carried out using the SHELXTL program package.

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References

1. J. Igbal, B. Bhatia, and N. Nayyar, *Chem. Rev.*, 1994, **94**, 519.
2. R. Kh. Freidlina, F. K. Velichko, S. S. Zlotskii, D. L. Rakhmankulov, and A. B. Terent'ev, *Radikal'naya telomerizatsiya* [*Radical Telomerization*] Khimiya, Moscow, 1988, 78 (in Russian).
3. M. S. Kharasch, O. Reinmuth, and W. H. Urry, *J. Am. Chem. Soc.*, 1947, **69**, 1105.
4. R. G. Gasanov, S. O. Videnskaya, L. V. Il'inskaya, Yu. N. Belokon', A. P. Pisarevskii, and Yu. T. Struchkov, *Dokl. Akad. Nauk*, 1994, **336**, 485 [*Dokl. Chem.*, 1994, **336** (Engl. Transl.)].
5. M. Asscher and D. Vofsi, *J. Chem. Soc.*, 1963, 1887, 3921.
6. R. Davis, J. L. A. Durrant, N. M. S. Khazal, and T. E. Bitterwolf, *J. Organomet. Chem.*, 1990, **386**, 229.
7. T. Suzuki and J. Tsui, *J. Org. Chem.*, 1970, **35**, 2982.

8. O. Gandolfi and M. Cais, *J. Organomet. Chem.*, 1977, **125**, 141.
9. M. Kameyama and N. Kamigata, *Bull. Chem. Soc. Japan*, 1987, **60**, 3687.
10. S. Murai, R. Sugise, and N. Sonoda, *Angew. Chem., Int. Ed. Engl.* 1981, **20**, 475.
11. M. Hajek, P. Silhavy, and B. Spirkova, *Coll. Czech. Chem. Commun.*, 1990, **55**, 2949.
12. C. J. Cable, H. Adams, N. A. Bailey, J. Crosby, and C. White, *J. Chem. Soc., Chem. Commun.*, 1991, 165.
13. E. Ts. Chukovskaya, R. G. Gasanov, I. I. Kandror, and R. Kh. Freidlina, *Zhurn. Vsesoyuzn. khim. obshch. im. Mendeleeva [Journal of the Mendeleev All-Union Chem. Soc.]* 1979, **24**, 161 (in Russian).
14. P. N. Hawker and M. V. Twigg, *Iron(II) and Lower States* in *Comprehensive Coordination Chemistry*, Ed. G. Wilkinson, Pergamon Press, Oxford; New York, 1987, **4**, 1179.
15. G. A. Gailyunas, G. V. Nurtdinova, V. P. Yur'ev, G. A. Tolstikov, and S. R. Rafikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, 914 [*Bull. Acad. Sci. USSR, Div. Chem.* Sci., 1982, **31**, 806 (Engl. Transl.)].
16. E. Nicolas, K. C. Russell, and V. J. Hruby, *J. Org. Chem.*, 1993, **58**, 766.
17. G. Li, K. C. Russell, M. A. Jarosinski, and V. J. Hruby, *Tetrahedron Lett.*, 1993, **34**, 2565.
18. B. H. Kim and D. P. Curran, *Tetrahedron*, 1993, **49**, 293.
19. D. A. Evans, K. T. Chapman, and J. Bisaha, *J. Am. Chem. Soc.*, 1988, **110**, 1238.
20. E. Wetss, K. Stark, I. E. Lankaster, and H. D. Murdoch, *Helv. Chim. Acta*, 1963, **46**, 288.
21. A. B. Terent'ev, S. I. Gapusenko, and T. T. Vasil'eva, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1418 [*Russ. Chem. Bull.*, 1993, **42**, 352 (Engl. Transl.)].
22. V. I. Tararov, T. F. Savel'eva, and Yu. N. Belokon', *Izv. Akad. Nauk, Ser. Khim.*, 1996, 649 [*Russ. Chem. Bull.*, 1996, **45**, 610 (Engl. Transl.)].
23. M. W. Wong, A. Pross, and L. Radom, *J. Am. Chem. Soc.*, 1994, **116**, 6284.
24. D. Grillor, J. M. Kanabus-Kaminska, and A. Maccol, *Teochem.*, 1988, **40**, 125.
25. F. G. Bordwell and A. V. Satish, *J. Am. Chem. Soc.*, 1994, **116**, 8885.
26. D. P. Curran and P. S. Ramamoorthy, *Tetrahedron*, 1993, **49**, 4841.
27. *Handbook of Chemistry and Physics*, 62nd ed., Ed. R. C. Weast, CRC Press Inc., Boca Raton, Florida, 1981—1982, F—181, 182.
28. Y. Ito, A. Sasaki, K. Tamoto, M. Sunagawa, and S. Terashima, *Tetrahedron*, 1991, **47**, 2801.
29. D. A. Evans and E. B. Sjogren, *Tetrahedron Lett.*, 1992, **33**, 2547.

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