Metal complex electrocatalytic reduction of 1,1-dihalocyclopropanes

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Catalytic electroreduction of several substituted *gem*-dihalocyclopropanes was studied in the presence of metal salen-complexes by polarography, cyclic voltammetry, and preparative electrolysis. Monohalocyclopropanes (54—59%) and the corresponding allene (5—9%) were the main reduction products. The reaction rate constants were determined. The inner-sphere electron transfer was shown to occur under these conditions.

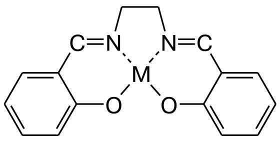
Key words: halocyclopropanes, allene, electrochemistry, catalysis, salen-complexes, kinetics.

Organic electrochemistry is permanently interested in mediator electrochemical processes. In addition to organic mediators, which are usually aromatic compounds with various structures,[1,2] metal salts and metal complexes[3,4] are widely used with this purpose. Metal salen-complexes,[5,6] which are also known as chiral catalysts for asymmetric oxidation,[7,8] have often been applied recently as catalysts of redox transformations of organics. However, their use as mediators in electrochemical redox processes is rather restricted and in nonelectrochemical reduction processes only single cases are known.[9] At the same time, it seemed promising to use salen-complexes as potential inductors of chirality in electrochemical reduction (ER) processes. Available data on the behavior of the metal salen-complexes during ER of the C—Hal bonds indicate that this process occurs ambiguously and often results in the formation of a variety of unsaturated compounds along with the dehalogenated product[5,6] and a substantial decrease in the yield of the latter. This is caused, as assumed,[10] by both the inner-sphere and outer-sphere electronic transfers in such systems, and the formation of the dehalogenation product is the result of the outer-sphere interaction. However, no special studies, capable of shedding light on specific features of ER processes involving metal salen-complexes, were performed until now.

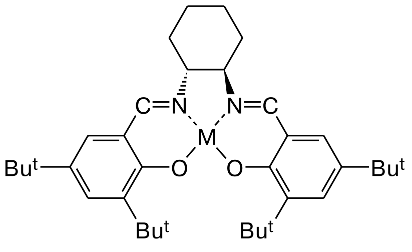
This stimulated us to state this work and study the electrocatalytic properties of salen-complexes of various metals during ER of the C—Hal bonds. 1,1-Dibromo- and 1,1-dichlorocyclopropanes were chosen as model substrates, although the data on their ER have been published,[11,12] because they allowed us to determine stereo-direction of the process under study.

Results and Discussion

Unsubstituted salen-complexes of some metals are used as mediators because they can reversibly be reduced.[13] However, it was necessary to reveal metals that form the salen complexes and conditions for the catalytic ER of dihalocyclopropanes to stop the process at the step of formation of monohalocyclopropanes. For this purpose, we synthesized *N*,*N*-bis(salicylidene)ethylenediamine (salen) and (*R*,*R*)-*N*,*N*-bis(3,5-di-*tert*-butylsalicylidene)cyclohexane-1,2-diamine (cgsalen) complexes of several metals. The electrochemical behavior of the complexes and their catalytic properties in ER processes of dihalo- and monohalocyclopropanes were characterized by the data of voltammetry and preparative electrolysis. The results are presented in Table 1.



M(salen)



M(cgsalen)

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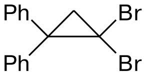
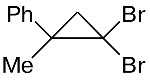
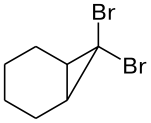
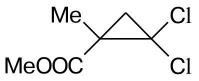
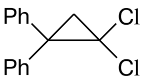
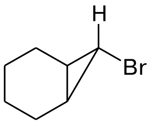
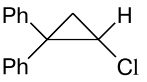
Table 1. Electrochemical characteristics of the reduction waves of the metal complexes, 1,1-dihalocyclopropanes, and monohalocyclopropanes in DMF/0.1 M Et_4NClO_4

Compound	$-E_{1/2}$/B[a]	n[b]	i_{an}/i_{cat}[c]	$2.3RT/(\alpha nF)$ /mV[d]
Zn(salen)	2.50	2.0	0.0	70
Ni(cgsalen)	2.26	1.0	0.50	73
Ni(salen)	2.07	1.0	0.56	62
Co(cgsalen)	1.94	1.0	0.73	63
Co(salen)	1.70	1.0	0.50	62
Cu(salen)	1.61	1.5	0.16	62
$Fe(salen)^+Cl^-$ [e]	0.75	1.0	—	63
	2.18	1.0		65
$Mn(cgsalen)^+Cl^-$ [e]	0.60	1.0	—	65
	1.81 2.68	2.0 2.0	0.0 0.0	160 140
	1.81 2.70	2.0 2.0	0.0 0.0	73 110
	1.96 2.88	2.0 1.9	0.0 0.0	130 130
	2.70	2.0	0.0	130
	2.81	2.0	0.0	120
	2.88	2.0	0.0	140
	3.13	2.0	0.0	100

[a] Against $Ag/AgNO_3$ (0.01 mol L^{-1}) in MeCN.

[b] Number of electrons determined by comparison with the one-electron wave of reduction of *p*-nitrobenzaldehyde.

[c] Ratio of the anodic commutated current to the limiting cathodic current, the switch-over frequency being 10 Hz.

[d] The angular coefficient of the wave was calculated by the formula $2.3RT/\alpha nF = (E_{3/4} - E_{1/4})/0.954$, where R is the universal gas constant, T is the absolute temperature, α is the transfer coefficient, n is the number of transferred electrons, and F is the Faraday number.

[e] The data were obtained by the CV method on the glass-carbon electrode.

All complexes are reduced in the accessible potential region. The Fe(salen)Cl and Mn(salen)Cl complexes react with mercury, and they were studied only by cyclic voltammetry (CV) on an inert glass-carbon electrode. The CV curves of Fe(salen)Cl exhibit two reversible one-electron reduction peaks corresponding to the transitions

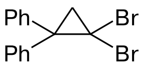
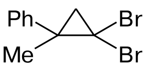
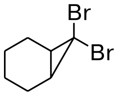
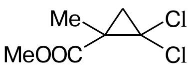
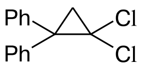
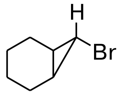
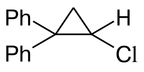
$$Fe(salen)^+ + e \rightleftharpoons Fe(salen),$$

$$Fe(salen) + e \rightleftharpoons Fe(salen)^-,$$

whereas the CV curve of Mn(salen)Cl contains one reversible peak of reduction of $Mn(salen)^+$ to Mn(salen). Electroreduction of other metal complexes was studied by classical and commutator polarography and cyclic voltammetry. The first reduction wave for Zn(salen) is irreversible, while that for Cu(salen) is quasi-reversible, indicating lability of anionic intermediates formed upon the one-electron reduction of these complexes. For all cobalt and nickel salen-complexes, the first reduction step affording anions of these complexes is one-electron and reversible. The cobalt complexes are reduced more easily than the corresponding nickel complexes. Di-*tert*-butyl-substituted salen-complexes are reduced less easily than the unsubstituted complexes because of the electron-donating effect of the *tert*-butyl substituents. As we have shown previously,[2] under polarographic conditions, dihalocyclopropanes undergo irreversible two-electron reduction to the corresponding monohalogen derivatives.

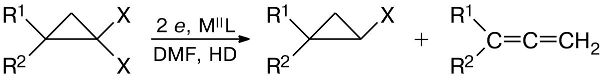
It follows from the data in Table 1 that the zinc salen-complexes cannot serve as mediators because their reduced forms are unstable. The nickel complexes are reduced more easily than dichlorocyclopropanes but less easily than dibromocyclopropanes and, therefore, can be used as catalysts only for dichlorides. No basic restrictions are known for the study of the catalytic properties of salen-complexes of other metals under study in the ER of mono- and dihalocyclopropanes. These complexes are reduced reversibly or quasi-reversibly and, hence, satisfy requirements imposed on mediators (electron carriers). The apparent rate constants of catalytic reduction of di- and monohalocyclopropanes by electrochemically generated anions of the metal salen-complexes are presented in Table 2. These constants were calculated using the polarographic and CV data from the catalytic increase in the limiting current of the wave and, correspondingly, the ER peak of the metal complex in the presence of halocyclopropane. The data in Table 2 show that the nickel(II), cobalt(II), and iron(II) salen-complexes are efficient mediators of ER of dichlorocyclopropanes, and the cobalt(II) complexes are also efficient in the ER of dibromocyclopropanes. The complexes of other metals are inactive under voltammetry conditions in the ER of both 1,1-dichloro- and 1,1-dibromocyclopropanes. Unlike monobromocyclopropanes, whose ER occurs with a high rate under voltammetry conditions, monochlorocyclopropanes are not reduced with a detectable rate by anions of the nickel and cobalt salen-complexes. In the case of Co(salen), the rate of this process is only eightfold lower than the ER rate of dibromocyclopropane. On the

Table 2. Apparent rate constants k_{app}/L mol^{-1} s^{-1} of the homogeneous reduction of halocyclopropanes by the electrochemically generated anions of salen-complexes of some transition metals* in DMF/0.1 M Et_4NClO_4

Metal complex	 [−1.81]	 [−1.81]	 [−1.96]	 [−2.70]	 [−2.81]	 [−2.88]	 [−3.13]
Ni(cgsalen) [−2.26]	—	—	—	16000	4500	490	—
Fe(salen) [−2.18]	—	—	—	—	3600	—	—
Ni(salen) [−2.07]	—	—	—	12000	3500	560	—
Co(cgsalen) [−1.94]	—	—	—	3500	3260	260	670
Co(salen) [−1.70]	22900	1550	4180	580	970	510	—

* The $E_{1/2}$/V are presented in brackets (see Table 1).

whole, dihalocyclopropanes exhibit a certain tendency for increasing the rate of their ER with an increase in the ER potentials of the complex and a decrease in the ER potentials of the substrate. This is natural for processes limited by the electron transfer rate. All metal salen-complexes obey the general regularity. In other words, according to the voltammetric data, di-*tert*-butyl-substituted complexes during ER of dihalocyclopropanes behave similarly to the unsubstituted analogs, *i.e.*, undergo no steric hindrance. The situation with ER of monobromonorcarane by the Ni(cgsalen) complex is somewhat different. In this case, the apparent rate constant of reduction is lower, which implies, most likely, a substantial steric effect of the chiral ligand on the kinetics.



X = Cl, Br; M = Ni, Co, Fe; L = salen, cgsalen

It is noteworthy that the apparent rate constants of reduction of dibromocyclopropanes, on the one hand, and monobromo- and dichlorocyclopropanes, on the other hand, by the Co(salen)$^-$ anions differ slightly. The difference in ER potentials for these groups of compounds is ~1.0 V, which is equivalent, according to the electrochemical kinetics laws, to the difference in rate constants of their heterogeneous ER (at $\alpha = 0.5$) by approximately eight orders of magnitude. At the same time, the rate constants of homogeneous reduction differ less than by two orders of magnitude (see Table 2).

We have previously[2] studied the ER of geminal dichloro- and dibromocyclopropanes using organic electron carriers as mediators, whose $E_{1/2}$ are less negative by 0.2—0.8 V than those of substrates. In this case, dichlorocyclopropanes are reduced *via* the outer-sphere electron transfer and dibromocyclopropanes are not reduced at all with the rate detectable by the polarographic method ($k \leq 10$ s^{-1}). The reduction rate of dichlorocyclopropanes increases substantially when the second mediator, *viz.*, transition metal complexes or ions, which act as inner-sphere electron carriers, is introduced in the solution.

As for the reduction of dichlorocyclopropanes by the salen-complexes, the rate of this process is by two—three orders of magnitude higher than the rate of reduction of these substrates by organic electron carriers at the same or even greater difference of mediator—substrate potentials. For example, the apparent rate constant of reduction of 2,2-diphenyl-1,1-dichlorocyclopropane by the 9,10-diphenylanthracene radical anions ($E_{1/2} = -1.99$ V) is 40 L mol^{-1} s^{-1}, while the rate of reduction by the Co(cgsalen)$^-$ anions is 3260 L mol^{-1} s^{-1}. These results indicate an energy gain at the electron transfer step for the metal complex reduction of dichloro- and dibromocyclopropanes compared to the reduction by organic carriers. The latter can be achieved only *via* the inner-sphere mechanism of transfer of electrons from the metal complex to the substrate.

The R—M—Hal σ-complex is the result of the primary electron transfer. In some cases, in particular, Ar—Ni—Br or Alk—Co—Hal, the σ-complex is reduced less easily than the metal complex, resulting in the appearance of a new reduction wave at more negative potentials.[14—16] In other cases (when the molecule contains an organohalogen substrate of acceptor substituents), the σ-complex is reduced at the same as the metal complex and even more positive potentials.[16]

No additional waves appear upon the metal complex ER of dihalocyclopropanes, and only an increase in the reduction wave of the metal complex is experimentally detected. This means that the σ-complexes are reduced at the same or less negative potentials.

The obtained data also show that under homogeneous conditions for both the outer- and inner-sphere mechanisms of electron transfer, unlike dichloro- and monobromocyclopropanes, dibromocyclopropanes are reduced with much lower rate than it could be expected based on the potentials of heterogeneous reduction of these substrates. Three reduction waves are observed in the voltammograms of 1,1-dibromo-2,2-diphenylcyclopropane detected on the Hg/Pt ultramicroelectrode at high substrate concentrations (0.1 mol L^{-1}). The first and last waves coincide with the polarographic reduction waves (Fig. 1). When the concentration of a depolarizer twofold increases, the height of the first wave remains unchanged and the subsequent two waves increase proportionally. Since the $E_{1/2}$ value on the mercury calomel electrode is much lower than on other electrodes, we can assume that the first wave on the Hg/Pt ultramicroelectrode is catalytic and corresponds to the reduction of dibromocyclopropane molecules adsorbed on the electrode. Then two subsequent waves can be considered, in the first approximation, as the successive two-step reduction of the initial compound from the nonadsorbed state. The difference between the $E_{1/2}$ values of the first and second waves ($\Delta E_{1/2}{}^{1,2}$ = 0.62 V) shows that the energy of adsorption of the cyclopropyl radical is ~64 kJ mol^{-1}. The ability of dibromocyclopropane to be reduced in chemical reactions in the solution bulk is represented by the reduction potentials of the nonadsorbed compound. This potential is by ~0.62 V more negative than the potentials of the first polarographic wave and is much closer to the reduction potentials of dichlorocyclopropanes. Therefore, the similarity of the rate constants of metal complex reduction of dibromo- and dichlorocyclopropanes is quite expected.

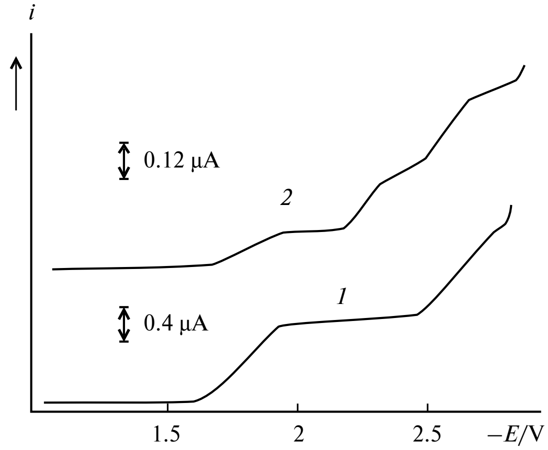
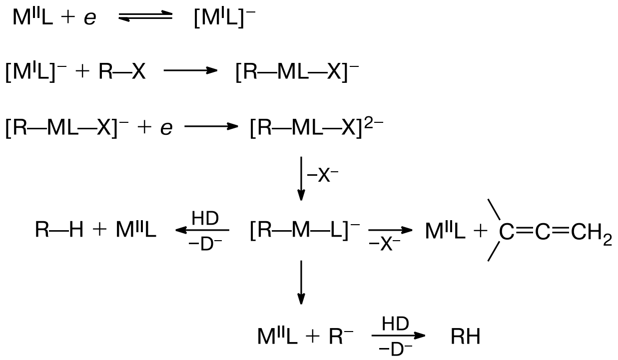


Fig. 1. Polarograms of the reduction of 1,1-dibromo-2,2-diphenylcyclopropane on a mercury calomel electrode ($C = 1 \cdot 10^{-3}$ mol L^{-1}) (*1*) and on a Pt/Hg ultramicroelectrode (radius of the ultramicroelectrode r = 5 μm, C = 0.1 mol L^{-1}) (*2*).

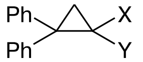
Based on the obtained results, we performed the preparative ER of 1,1-dichloro-2,2-diphenylcyclpropane and 1,1-dibromo-2,2-diphenylcyclopropane in DMF using the nickel and cobalt catalysts on the carbon-tissue electrode. The process was catalytic during the whole electrolysis and the loss of metal complexes was insignificant, which follows from the data on permanent polarographic monitoring of the reaction mixture composition. The results of electrolysis are presented in Table 3. In all cases, monohalocyclopropanes (54—59% yield) and allene (5—9%) are the main ER products. Similar results were obtained for the reduction on the mercury electrode and the use of an alcohol or phenol as a proton donor. The formation of the reaction products can be described by Scheme 1.

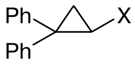
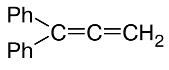
Scheme 1



In addition, the fragments $Ph_2C{=}CHCH_3$ (*m/z* 194), $Ph_2C{=}CPh_2$ (*m/z* 332), diphenyl (*m/z* 154), and $Ph_2C{=}CH_2$ (*m/z* 180) were detected in minor amounts by mass spectrometry for 1,1-dichloro-2,2-diphenylcyclopropane. The reduction of 1,1-dibromo-2,2-diphenylcyclopropane does not afford these compounds producing only two by-products with molecular weights 116 and 234. In the case of the chiral Co(cgsalen) metal com-

Table 3. Results of the preparative electroreduction of 1,1-dihalo-2,2-diphenylcyclopropanes and 1-chloro-2,2-diphenylcyclopropane



X	Y	$M^{II}L$	I/mA	Yield (%)	
					
Cl	Cl	Co(salen)	25	54	6
		Ni(salen)	25	54	6
		Co(cgsalen)	8	59	9
		Ni(cgsalen)	25	57	8
Br	Br	Co(salen)	25	54	5
H	Cl	Ni(cgsalen)	8	32	0

plex, chirality of monochlorocyclopropane is not virtually induced. According to measurements of the specific rotation, the enantiomeric excess *ee* does not exceed 2%. It is not clear from the obtained date which species is protonated ([R—M—L]$^-$ or R$^-$) and whether chirality is lost at the protonation step. To solve this problem on asymmetric induction by chiral metal complexes in principle, a possible influence of the protonation step should be excluded at the initial stage. We believed that it could be done in the case of a racemic mixture of nonsymmetrical dichloro- or monochlorocyclopropanes if the reaction is performed by 50% and the process is monitored by the remained amount of dichloro- or monochlorocyclopropane. This reduction was carried out for 1-chloro-2,2-diphenylcyclopropane using the chiral Ni(cgsalen) complex as a catalyst (see Table 3). In this case, chirality is not induced. This suggests, most likely, that the chirality of the substrate is not induced in the step of electron transfer from the metal complex to halocyclopropanes under the conditions used.

It should be mentioned in conclusion that the results of kinetic studies suggest the efficient inner-sphere mechanism of reduction of 1,1-dihalocyclopropanes by the electrochemically generated salen-complexes of metals in the low oxidation state. We did not find any indications of the possibility of the outer-sphere mechanism of the reaction. In this case, the allene to monohalocyclopropane ratio in the ER products is determined by the ratio of rates of competitive reactions of elimination of the second halide ion and protonation of anionic intermediates rather than by the different mechanism of electron transfer from the catalyst to substrate, as it was assumed when the chromium ions were used.[10]

Experimental

Electrochemical reduction of 1,1-dihalocyclopropanes was studied by classical and commutator polarography, cyclic voltammetry, and electrolysis in DMF against Et_4NCl (0.1 mol L^{-1}). Polarograms were recorded on a PU-1 polarograph. The characteristics of the capillary were the following: $m = 0.71$ mg s^{-1}, $t_1 = 0.5$ s. An LP 7e polarograph with a switch-over frequency of 10 Hz was used as an auxiliary instrument for recording commutated curves. Polarization curves on the Pt ultramicroelectrode ($r = 5$ μm), on which mercury was electrochemically deposited (Pt/Hg ultramicroelectrode) were recorded using a GWP 673 polarograph. Cyclic voltammograms were detected using a PI-50-1 potentiostat on a glass-carbon disk electrode (2 mm in diameter) molded in Teflon. The potential sweep was 100 mV s^{-1}. A silver Ag/AgNO$_3$ electrode in MeCN (0.01 mol L^{-1}) served as a reference electrode (E_0(Fc/Fc$^+$) = +0.16 V), and a Pt wire was used as an auxiliary electrode. The solution was deaerated by nitrogen. The concentration of the substrate in polarographic measurements was $1 \cdot 10^{-3}$ mol L^{-1}, and that for recording cyclic voltammograms was $3 \cdot 10^{-3}$ mol L^{-1}, the temperature being 298 K. Apparent rate constants of mediatory reduction of halocyclopropanes were determined by polarography using the Bendersky—Mairanovsky approximating formula[17] and by CV using the Nicholson correlation.[18] Procedures of purification of solvents and supporting salts and methods of polarographic measurements have been described previously.[19] Metal salen-complexes were synthesized by known methods.[20—26] Halocyclopropanes were synthesized from the corresponding olefins and haloform using the Makosza method.[27—29]

NMR spectra were recorded in $CDCl_3$ on Varian T-60 (^{1}H, 60 MHz) and Bruker MSL-400 (^{13}C, 100.62 MHz) spectrometers using $CDCl_3$ and Me_4Si as internal standards. IR spectra were obtained on an UR-20 spectrometer in Nujol. Optical rotation was determined on a Perkin—Elmer 341 polarimeter with a sodium lamp (λ = 589 nm).

Electrochemical reduction of 1,1-dihalo-2,2-diphenylcyclopropanes was carried out using a B5-70 power pack in a diaphragm (cellulose) electrolyzer using a Hg pool as a cathode and a Pt wire as an anode in the galvanostatic regime ($I = 25$ mA). A working solution (20 mL) was prepared by dissolution of Et_4NCl (0.1 mol L^{-1}), 1,1-dihalocyclopropane (1.9 mmol), metal salen-complex (0.19 mmol), EtOH (0.5 mL), and phenol (1.9 mmol) in DMF. The reaction course was monitored by GLC-MS on a MAT-212 instrument using an SI-54 column (50 m × 0.3 mm). During the reaction, chromatograms of the reaction mixture were recorded by the total ion current and mass spectra were detected at the chromatographic peaks, Mass spectra (EI) were recorded in an interval of 40—500 *m/z* with a recording rate of decade s^{-1}. The regime of mass spectra recording: ionizing voltage 70 V, emission current 0.5 A, resolution 1000, and temperature of the source 120 °C. Chromatographic regime: temperature of the injector 240 °C, programmed temperature change (6 deg min^{-1}) from 100 (6 min) to 240 °C (30 min), and helium as the carrier gas. Petroleum ether in the concentration ~1% was used as a solvent of reaction mixture samples. Recording of chromatograms and mass spectra was started 5 min after sample injection to cut off the peak of the solvent.

After the end of electrolysis, water (20 mL) was added to the reaction mixture, and the resulting mixture was extracted with hexane (3×20 mL). The combined organic layers were washed with water and dried with Na_2SO_4. After the solvent was distilled off, the residue was separated by column chromatography on silica gel using hexane as the eluent. The yields of the obtained compounds are presented in Table 3. The characteristics of 1-chloro-2,2-diphenylcyclopropane coincide with the published data.[30]

1,1-Diphenylallene. ^{1}H NMR, δ: 5.22 (s, 2 H, =CH$_2$); 6.90—7.60 (10 H, 2 Ph). ^{13}C NMR, δ: 78.06 (=CH$_2$); 127.37 (*p*-CH); 128.63 (*o*-CH); 128.56 (*m*-CH); 136.56 (Ph$_2$C=); 142.30 (C$_{ipso}$); 210.14 (=C=). IR, ν/cm^{-1}: 853 (=CH$_2$); 1934 (C=C=C); 1598 (Ph); 1492 (C=O).

Electrochemical reduction of 1-chloro-2,2-diphenylcyclopropanes and further treatment of the reaction mixture were carried out using a procedure similar to that described above in the galvanostatic regime at a current of 8 mA. The amount of the passed electricity was 2.1 *F* mol^{-1}. The starting 1-chloro-2,2-diphenylcyclopropane was separated from the reaction products by column chromatography on silica gel (hexane as an eluent) and analyzed polarimetrically.

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