# ELECTROCHEMICAL REDUCTION OF 1,1-DIHALO-2,2-DISUBSTITUTED CYCLOPROPANES

**Yu. M. Kargin, E. I. Gritsenko, V. V. Yanilkin, V. V. Plemenkov, L. K. Dubovik, N. I. Maksimyuk, B. M. Garifullin, Sh. K. Letypov, and A. V. Il'yasov**

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*The electrochemical reduction of 1,1-dihalo-2-R-2-methylcyclopropanes was studied by polarography and preparative electrolysis. A mixture of stereoisomeric monoboro- and monochlorocyclopropanes was obtained with preparative yield of 60-70% in preparative electroreduction in methanol against a background of 0.1 M $LiClO_4$. In the case of bromine derivatives of cyclopropanes (except when R = CN) an effect was found on the part of the current density on the ratio of cis and trans isomers, which was interpreted as a change, in dependence on current density, of the contributions of the reactions of reduction of the starting compounds ($S_N2$ mechanism) and ionic pairs ($S_N1$ mechanism). The effect of the solvent ($CHCl_3$, DMF, DMSO, MeOH) and background salt ($LiClO_4$, $Et_4NBr$) on the ratio of stereoisomers is in agreement with this interpretation.*

***Keywords:*** *electroreduction, stereoisomer, potential, cyclopropane, electrolysis.*

The reactions of electron transfer involving substituted *gem*-dihalocyclopropanes are drawing attention not only in connection with the possible synthetic development of these processes, but also with insufficient clarity about the stereochemical aspects of the functionalization of the cyclopropane synthon [1, 2]. There are a number of disputed matters in the mechanism of the electrochemical rupture of the carbon–halogen bond for which an explanation would aid in the development of stereoselective methods of electrochemical synthesis.

## EXPERIMENTAL

1,1-Dihalo-2-R-2-methylcyclopropanes (**1-7**) [Hal=Br, R=Me (**1**), CH=$CH_2$ (**2**), CMe=$CH_2$ (**3**), Ph (**4**), COOMe (**5**), CN (**6**); Hal=Cl, R=COOMe (**7**)] were synthesized by conventional techniques [3-5] and purified by vacuum distillation. Dimethylformamide was purified in accordance with [6]. The background electrolyte for polarography was a 0.1 *M* solution of $Bu_4NI$ in DMF. The polarograms were recorded on an LP-7e polarograph. The characteristics of the capillary were: $m$ = 0.17 mg/sec and $t$ = 0.5 sec. The switching frequency was 10 Hz. Measurements were made at 25°C. The potentials in this paper are reported relative to the bottom mercury, which had a potential of −0.5 V relative to a saturated calomel electrode.

Preparative reduction of **2-7** (0.1 *M*) was accomplished with a P-5827 potentiostat in galvanostatic mode in a membrane electrolyzer at 20°C. The background electrolyte in the case of dibromocyclopropanes **2-6** consisted of 0.1 *M* solutions of $LiClO_4$ and $Et_4NI$ in various solvents (MeOH, 70% aqueous MeOH, DMF, $CHCl_3$, DMSO). The catholyte volume was 80 ml and the cathodes used were Cu/Hg, Cu, Ni ($S_{cat}$ = 63 $cm^2$). The anolyte volume was 20 ml and the anode was a Pt grid. Added to the anode compartment was 5 ml $N_2H_4 \cdot H_2O$. The process was accomplished in a continuous stream of argon and with mixing of the reaction mixture. In every case the amount of electricity passed through the cell was 2 F/mole. After completion of electrolysis 100 ml $CH_2Cl_2$ and $H_2O$ were added to the catholyte. The aqueous layer was treated with another portion of $CH_2Cl_2$. The combined organic layers were washed with water and dried with $CaCl_2$. After driving off the solvent the products of electrosynthesis were purified by vacuum distillation. The physicochemical constants of the product monohalocyclopropanes correspond to literature data [3, 5, 7]. The *cis* and *trans* isomers of 1-bromo-2-methyl-2-cyanocyclopropane (**13**) were separated by vacuum distillation ($T_{bp}$ (*trans*) 75°C/12 mm Hg, $T_{bp}$ (*cis*) 92°C/12 mm Hg [5]).

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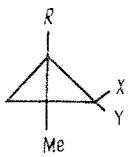
TABLE 1. Electrochemical Characteristics of Reduction Waves of 1,1-Dihalocyclopropanes and Monobromocyclopropanes in DMF against a Background of 0.1 *M* $Bu_4NI$




| R | X | Y | $-E_{1/2}$, V | $\frac{\Delta E/}{/\Delta \lg \frac{i}{ij-i}}$, mV | $I_{in}^{\times 10^6}$, A * |
|---|---|---|---|---|---|
| Me | Br | Br | 1.28 | 187 | 0.83 |
| | | | 2.35 | 230 | 0.84 |
| CH=CH | Br | Br | 1.21 | 178 | 0.82 |
| | | | 2.25 | 220 | 0.82 |
| CMe=CH | Br | Br | 1.25 | 168 | 0.85 |
| | | | 2.30 | 225 | 0.85 |
| Ph | Br | Br | 1.19 | 160 | 0.87 |
| | | | 2.23 | 220 | 0.89 |
| COOMe | Br | Br | 0.87 | 137 | 0.85 |
| | | | 2.01 | 157 | 0.85 |
| CN | Br | Br | 0.64 | 109 | 0.83 |
| | | | 1.85 | 251 | 0.83 |
| COOMe | Cl | Cl | 2.07 | 200 | 0.90 |
| Ph | H | Br | 2.21 | 230 | 0.85 |
| COOMe | H | Br | 1.98 | 125 | 0.94 |
| CN | Br | H | 1.88 | 230 | 0.92 |
| CN | H | Br | 1.62 | 190 | 0.92 |

*Limiting current of one-electron reduction wave of benzophenone is $0.42 \cdot 10^6$ A.

NMR spectra were recorded on a Bruker WM-250 instrument: SF($^1$H) = 250.132 mHz; SF($^{13}$C) = 62.9 mHz; SI = 16 K; PW($^1$H) = 1 sec; RD($^1$H) = 5 sec; PW($^{13}$C) = 7 sec; RD($^{13}$C) = 3 sec.

## RESULTS AND DISCUSSION

Two waves of equal height are seen on the polarograms of dibromocyclopropanes **1-6**. One reduction wave is registered in the case of **7**. The electrochemical characteristics of the reduction waves are given in Table 1. All waves are irreversible, which is indicated by the absence of anode current on the commutated curves in the region of reduction potentials. The value of the limiting current of the wave in each case corresponds to transfer of two electrons per molecule. The polarograms of the monohalocyclopropanes have one two-electron reduction wave, with the half-wave potential of the second wave of the dihalocyclopropanes (Table 1). This fact is evidence that the first polarographic wave of the dihalocyclopropane corresponds to the process of its reduction to monohalocyclopropane, while the second wave corresponds to electrochemical rupture of the second C–Hal bond.

The half-wave potentials of the first and second waves of the dihalocyclopropanes are dependent both on the nature of the halogen and on the nature of the substituents on $C^2$. Dibromocyclopropanes are reduced much more easily than the corresponding dichlorocyclopropanes. In the series **1-6** the reduction process becomes much easier as one moves from compound **1** to compound **6**. The substantial difference of potentials of the first and second waves ($\Delta E$ = 1.1-1.2 V) is striking. This opens up the possibility of a relatively simple electrosynthesis of monobromocyclopropanes under conditions in which potential is monitored. Only one reduction wave is recorded in the case of **7**. The two-electron nature of this wave suggests the possibility of electrochemical synthesis of monochlorocyclopropane.

Preparative electroreduction of **2-7** on an copper amalgam electrode was carried out at various current densities. The results of electrolysis in methanol against a background of 0.1 *M* $LiClO_4$ are given in Table 2.

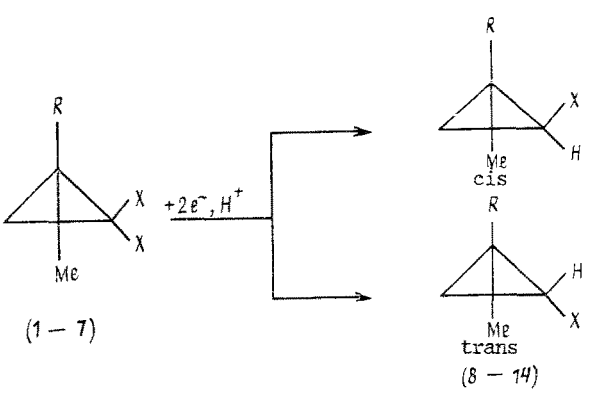
TABLE 2. Electrochemical Reduction of 1,1-Dihalocyclopropanes **2-7** in Methanol on a Copper Amalgam Electrode against a Background of 0.1 *M* $LiClO_4$

| Compound | *I*, A | Ratio of cis to trans isomers | Yield, % |
|---|---|---|---|
| **2** | 0.1 | 1.9 : 1 | 47.8 |
| | 1.0 | 3.4 : 1 | 48.3 |
| **3** | 0.1 | 1.3 : 1 | 68.4 |
| | 1.0 | 2.2 : 1 | 66.7 |
| **4** | 0.1 | 1 : 1.2 | 64.7 |
| | 1.0 | 5.5 : 1 | 63.8 |
| **5** | 0.1 | 1 : 1.4 | 44.4 |
| | 0.3 | 1 : 1.4 | 71.8 |
| | 0.6 | 1.7 : 1 | 63.4 |
| | 1.0 | 2.3 : 1 | 56.4 |
| | 1.0 * | 1 : 1 | 61.7 |
| **6** | 0.1 | 6 : 1 | 66.8 |
| | 0.6 | 5 : 1 | 81.7 |
| | 1.0 | 5.3 : 1 | 79.3 |
| **7** | 0.1 | 3.5 : 1 | 60.2 |
| | 0.5 | 3.5 : 1 | 63.4 |
| | 1.0 | 3.5 : 1 | 61.3 |

*Dibromocyclopropane was added periodically in the course of the entire electrolysis process; its initial concentration in the solution was 0.01 *M*. Electrolysis was conducted at the potentials of the limiting current.

According to $^1H$ NMR spectroscopy, the electrolysis processes in all cases are characterized by conservation of the three-member ring. Their preparative yield is 60-70%. The spectrum of each product is represented by a double set of signals of three protons of the ring, which is evidence of the formation of two stereoisomeric monobromocyclopropanes **9-14**. Structural identification of the latter was done by $^{13}C$ and $^1H$ NMR methods.

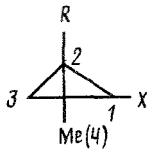
**Scheme 1**




X=Br, R=Me (**1, 8**); CH=$CH_2$ (**2, 9**); CMe=$CH_2$ (**3, 10**); Ph (**4, 11**); COOMe (**5, 12**); CN (**6, 13**); X=Cl, R=COOMe (**7, 14**).

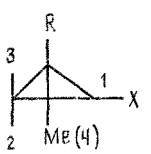
It is well-known that $^{13}C$ NMR spectroscopy is an effective method for establishing the conformation structures of organic compounds in solutions. Therefore, we determined the isomeric composition on the basis of analysis of the $\gamma$ effect of bromine on the signals of methyl and substituents in position 2 in various forms. The data for most of the compounds agree with the literature data (the slight disagreement from the data of [5, 8] is probably due to effects of the solvent). As was assumed, the effect of strong-field displacement of signals when bromine is in *cis* position to both Me and to the substituent in position 2 is significant and is characteristic (Table 3).

TABLE 3. $^{13}C$ NMR Spectral Characteristics of Compounds **9-15** [solvent $CCl_4$ + 10% $CDCl_3$; chemical shifts measured relative to $\sigma(CDCl_3)$ = 77.0 ppm; $\Delta\sigma$ = ±0.03 ppm; $T$ = 298 K]




| Compound | X | R | C¹ | C² | C³ | C⁴ | Signals of R |
|---|---|---|---|---|---|---|---|
| cis-9 | Br | CH=CH | 29.60 | 23.20 | 24.07 | 20.77 | 141.43(CH)<br>114.00(CH) |
| trans-9 | Br | CH=CH | 30.10 | 23.00 | 23.51 | 19.16 | 142.28(CH)<br>112.49(CH) |
| cis-10 | Br | CMe=CH | 27.15 | 28.57 | 22.36 | 23.37 | 145.38(CH)<br>114.12(CH)<br>20.40(CH) |
| trans-10 | Br | CMe=CH | 29.01 | 27.34 | 22.66 | 21.21 | 147.07(CH)<br>111.21(CH)<br>20.40(CH) |
| cis-11 | Br | Ph | 27.92 | 27.57 | 22.19 | 27.16 | 129.34<br>128.14<br>126.76<br>141.99(C) |
| trans-11 | Br | Ph | 30.27 | 25.83 | 23.33 | 24.10 | 128.52<br>126.96<br>126.49<br>144.34(C) |
| cis-12 | Br | COOMe | 25.34 | 26.51 | 22.17 | 19.75 | 51.74(OMe)<br>170.07(CO) |
| trans-12 | Br | COOMe | 28.34 | 23.48 | 24.91 | 16.78 | 52.00(OMe)<br>172.50(CO) |
| cis-13 | Br | CN | 22.25 | 14.36 | 24.24 | 20.39 | 119.67 |
| trans-13 | Br | CN | 25.36 | 9.57 | 23.30 | 18.33 | 120.40 |
| 15 | H | Ph | 15.63 | 20.04 | 15.63 | 26.16 | 128.20<br>126.87<br>125.55<br>146.75(C) |

TABLE 4. $^{1}H$ NMR Spectral Parameters of Compounds **9-15** (solvent $CDCl_3$, $\sigma$ = 7.24 ppm, $T$ = 298 K)




| Compound | H¹ | H² | H³ | Me⁴ | R |
|---|---|---|---|---|---|
| cis-9 | 2.977 | 1.213 | 1.041 | 1.229 | 5.782; 5.162; 5.111 |
| trans-9 | 2.814 | 0.913 | 1.362 | 1.362 | 5.474; 5.008; 4.956 |
| cis-10 | 2.806 | 1.150 | 1.103 | 1.205 | 4.939; 4.828 |
| trans-10 | 2.978 | 1.395 | 0.773 | 1.351 | 4.741; 4.715 |
| cis-11 | 3.073 | 1.370 | – | 1.442 | ~7.3 |
| trans-11 | 3.207 | 1.638 | 1.054 | 1.596 | ~7.3 |
| cis-12 | 2.916 | 1.775 | 1.213 | 1.363 | 3.729 |
| trans-12 | 3.482 | 1.818 | 0.979 | 1.449 | 3.656 |
| cis-13 | 2.890 | 1.536 | 1.426 | 1.452 | – |
| trans-13 | 3.434 | 1.852 | 1.074 | 1.526 | – |
| 15 | | | 0.86(*m*)<br>0.82(*m*) | 1.340(*s*) | 7.3–7.05(*m*) |

Analysis of the $^1H$ NMR data in the literature for the investigated compounds showed that most of them do not give an attribution of the $^1H$ NMR parameters of the individual isomers (the cyano derivatives are an exception). Therefore, we made a correlation of the $^{13}C$ and $^1H$ (CW heteroresonance) NMR parameters by means of determining the spectral parameters of all of the investigated compounds in both isomeric structures (Table 4). The quantitative isomer ratio was determined from a comparison of the integral intensities of the corresponding protons of the isomeric forms.

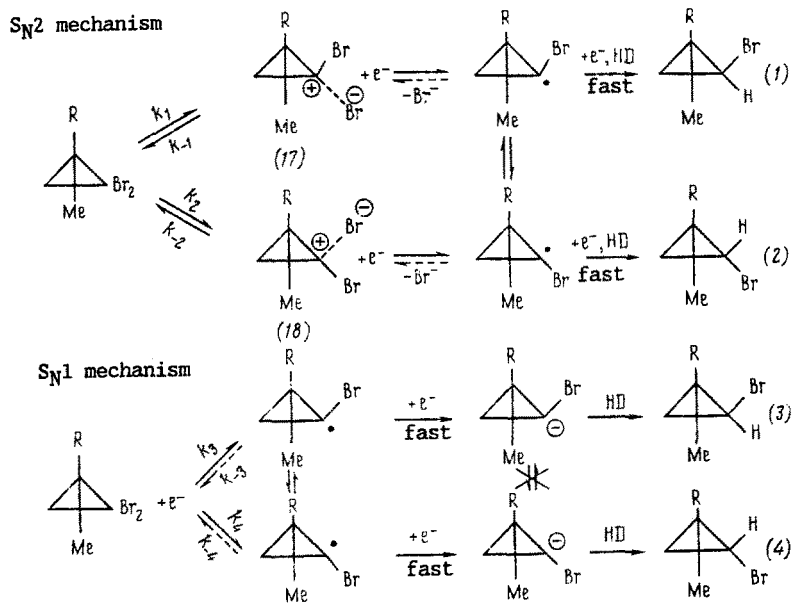
As can be seen from Table 2, in the reduction of **7** and dibromocyclopropane with a substituent having clearly expressed electron-acceptor properties (compound **6**) the current density does not have a significant effect on the stereospecificity of the

process: at all current densities, primarily the *cis* isomer is formed. However, in the case of the other dibromocyclopropanes when methanol was used as solvent there was a significant effect of current density on the stereoselectivity of the reduction process. Thus, at high current densities there was an increase of the share of the *trans* isomer.

The irreversible nature of the electrochemical process of dehalogenation and the detection of an effect on the part of current density on the ratio of isomeric monohalo derivatives suggests that the formation of products is to a significant degree kinetically controlled.

A mechanism that incudes synchronous transfer of an electron and rupture of the C–Hal bond, i.e., an $S_N2$ mechanism, is assumed in the literature [9] in the electrochemical reduction of haloorganic compounds. The facilitating action of electron-acceptor substituents in the reduction of dihalocyclopropanes is in agreement with this mechanism.

**Scheme 2**




In contrast to monohaloorganic compounds, in this case it is possible for there to be competing monodebromination and inversion of radicals and carbanions (Scheme 2). The irreversible character of the electrochemical process of dehalogenation and the experimentally detected effect of the current density (potential) on the ratio of isomeric products suggests that the formation of products is to a significant degree kinetically controlled. Otherwise, the isomeric composition of the products would be determined by the relative preference for formation of one of the two isomers and would be completely the same for any value of current density. However, the extremely slow inversion of the cyclopropyl carbanions [10] and their rapid protonization are evidence of the absence of equilibrium among carbanion particles. The yield of *cis*- and *trans*-monohalocyclopropanes according to this scheme ($S_N2$ mechanism) will be determined by the ratio of the reaction rates of electron transfer and inversion of radicals.

A comparison of the half-wave potentials of the reduction of the *cis* and *trans* isomers of CN-substituted monobromocyclopropane shows that the *trans* isomer is reduced more easily, i.e., rate constant $k_3$ of electron transfer with subsequent *trans*-elimination of the Br ion is higher than $k_4$. The rate constant of transfer of the second electron is higher than the rate constant of transfer of the first electron and at high current densities (potentials) the contribution of the process of

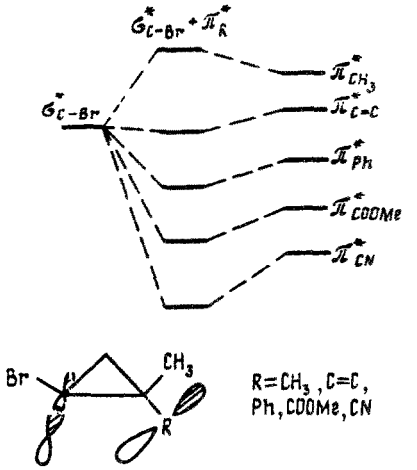



Fig. 1. Schematic drawing of LUMO for the series of dibromocyclopropanes.

TABLE 5. Electrochemical Reduction of 1,1-Dibromo-2-carbomethoxy-2-methylcyclopropane

| Solvent | Cathode material | Background salt | *I*, A | Ratio of cis to trans isomers |
|---|---|---|---|---|
| MeOH | Cu/Hg | $LiClO_4$ | 0.3 | 1 : 1.4 |
| MeOH | Cu/Hg | $Et_4NBr$ | 0.3 | 1 : 1 |
| MeOH | Cu | $LiClO_4$ | 0.3 | 1 : 1.4 |
| MeOH | Ni | $LiClO_4$ | 0.3 | 1 : 1.6 |
| $CHCl_3$ | Cu/Hg | $LiClO_4$ | 0.3 | 2 : 1 |
| DMF | Cu/Hg | $LiClO_4$ | 0.6 | 1.7 : 1 |
| DMSO | Cu/Hg | $LiClO_4$ | 0.3 | 1.9 : 1 |

inversion is negligible and, therefore, the preferential formation of the *cis* isomer in the reduction of dibromocyclopropane **6** is consistent with theory. Since the substituents on $C^2$ are also electron-acceptor substituents in the case of the other cyclopropanes, as follows from the smaller value of $E_{1/2}$ by comparison with **1**, in all cases one should preferentially obtain the *cis* isomer at high current densities if the process follows the same mechanism under all experimental conditions. The high value of the rate constant of electron transfer and *trans*-elimination of the Br ion is probably connected with the lower energy of the free orbital $\sigma^*$ because of effective stabilizing action of the $\sigma^*(C-Br)$ and $\pi^*(R)$ levels (Fig. 1).

With a decrease of the current density there is a decrease of the rate constant of the steps of electron transfer and an increase of the contribution of the process of radical inversion and, therefore, there may be an increase of the yield of the *trans* isomer. The effect of the current density (potential) on the ratio of *cis* and *trans* isomers can be explained in this way. However, within the framework of this scheme it is difficult to explain the preferential formation of the *trans* isomer at low current densities for compounds **4** and **5** or the independence of the *cis/trans* ratio for compound **6**.

At lower current densities a different process mechanism may make a significant contribution to the distribution of products. The effect of adsorption on the *cis/trans* ratio is discussed in [11]. It might be thought that in the reduction of these compounds some part of the substance is reduced from the adsorbed state with preferential formation of the *trans* isomer. However, there are not sufficient arguments in favor of this hypothesis. First, the peaks that are normally observed in the adsorption of a depolarizer are not present on the polarograms. Second, special experiments with cathodes made of different materials show that the electrode material does not have a significant effect on the isomer ratio (Table 5). The very same ratio of isomers is obtained on copper amalgam, copper, and nickel cathodes in the electroreduction of compound **5** at low current densities. Then, in the reduction of compound **5** at limiting current potentials the ratio of isomers is close to 1 (Table 2), which can be attributed only to absence of an orienting effect on the part of the electrode material and identical diffusion-controlled rate of rupture of both C–Br bonds. In addition, the independence of the isomer ratio on current density in the reduction of **7** is evidence that adsorption does not have a significant effect on the stereochemical result of electrolysis.

The ion-pair mechanism [12] is widely used in the interpretation of the results of nucleophilic substitution reactions. The calculations of [12] show that dissociation not only of tertiary, but also of primary, alkyl halides is thermodynamically

allowed. Dihalocyclopropanes participate in nucleophilic substitution reactions with difficulty and this probably indicates only polarization of the C−Br bond in formation of some quantity of ion pairs that are reduced more easily than the starting compounds ($S_N1$ -like mechanism). When there is simultaneous reduction of molecular forms and ion pairs the overall process can be represented by Scheme 2.

Here the *cis/trans* ratio will be determined by the rates of reactions (1)-(4). Reactions (1) and (3) lead to the formation of the *cis* isomer, while reactions (2) and (4) lead to the *trans* isomer. The preferential realization of one or the other direction of reduction is probably determined by the same conditions as in chemical reactions of nucleophilic substitution — by the nature of the substituent, the solvent, and the background salt, by the ability of substituents to stabilize an intermediate of one or another structure, and so forth. In addition, since this question is electrochemical, the ratio of products via these two mechanisms is dependent to a significant degree on the electrode potential (the current density). Quite different variations are possible, but we will only discuss some of them, the ones that are most likely to be realized in the reduction of dihalocyclopropanes.

1. If electrolysis is conducted at the potentials of the limiting diffusion current $I = E_{lim}$ ($i = i_{lim}$), in this case the rates of reactions (3) and (4) are equal to $v_{dif}/2$ and according to the $S_N2$ mechanism the *cis/trans* ratio is 1:1. According to the $S_N1$ mechanism, this ratio will be determined by the ratio of equivalent volume concentrations of ion pairs **17** and **18**. The substituents on $C^2$ exhibit electron-acceptor properties and without question will impede the formation of ion pairs. Since their effect develops to a greater degree in *trans* position, it is obvious that the equilibrium concentration of form **18**, which leads to the formation of the *trans* isomer, will be higher than that of form **17**. The dihalocyclopropanes are probably characterized by low degrees of dissociation and, therefore, the reduction of the ion pairs will be negligible and the ratio of isomeric products will be close to 1.

2. If electrolysis is conducted at potential $E < E_{lim}$ ($i < i_{lim}$), then the process rate according to the $S_N1$ mechanism is limited by the rate of the chemical reaction of dissociation, while according to the $S_N2$ mechanism it is limited by electrochemical kinetics. The first reaction is chemical and the reaction rate is determined probably by the same conditions as in the chemical reactions of nucleophilic substitution, but it is not dependent on potential, while the rate of electron transfer according to the $S_N2$ mechanism is exponentially dependent on potential. Because of the electron-acceptor properties of the substituents on $C^2$ and their different influences in *cis* and *trans* position ($k_1 > k_2$, $k_3 > k_i$), according to the $S_N1$ mechanism the trans-isomer should be obtained preferentially. According to the $S_N2$ mechanism, conversely, the *cis* isomer should predominate in the products. Therefore, as one moves from higher current densities to lower ones, there is an increase of the contribution of the $S_N1$ process and correspondingly the yield of *trans* isomer increases.

3. If electrolysis is conducted at potential $E_2 < E_1$ ($_2 < i_1$), the process rate according to the $S_N1$ and $S_N2$ mechanisms is limited by electrochemical kinetics. In this case the ratio of *cis* and *trans* isomers will be a complex function of all the rate constants of the reactions shown in Scheme 2. However, considering that $k_5 > k_6$, one can suggest that there should be an increase of the share of the *cis* isomer as one moves from $E_1$ to $E_2$ (from $i_1$ to $i_2$).

Thus, this analysis shows that in the case of parallel reduction according to $S_N1$ and $S_N2$ mechanisms while varying the current density in a wide range from $i_{lim}$ to minimum values the ratio of *cis* and *trans* isomers can take on quite varied values. The preferable formation of the *cis* isomer according to the $S_N2$ mechanism is evidently connected with the greater electron-acceptor character of the C−Br bond of the halogen atom in *trans* position to the R substituent, since it is in this position that there is the effective stabilizing interaction of the $\sigma^*$(C−Br) and $\pi^*$(R) levels (Fig. 1). The experimental data are in agreement with the proposed reduction scheme. In the preparative reduction of compound **5** at a current density corresponding to the limiting diffusion current the ratio of *cis* and *trans* isomeric monobromocyclopropanes is 1:1. On transition to the region of kinetic control ($i$ = 1A) the process in all cases preferentially follows the $S_N2$ mechanism, and the *cis* isomer predominates in the products. With a decrease of the current density the contribution of the $S_N2$ mechanism increases, the contribution of the $S_N1$ mechanism decreases, and correspondingly the yield of the *cis* isomer decreases. The only exceptions are compounds **6** and **7**, for which the ratio of *cis* and *trans* isomers is not dependent on the current density.

The type of substituent has a significant effect on the preference for realization of one of the two mechanisms in question. Thus, the $S_N1$ mechanism is suppressed to a significant degree under the effect of electron-acceptor substituents, which impede heterolysis of the C−Hal bond. This shows up particularly clearly in the case of cyanocyclopropane **6** and the reduction process at all current densities follows the $S_N2$ mechanism. Moving to substituents with less-pronounced electron-acceptor properties (aryl, alkyl, alkenyl), the capacity of the latter for $S_N1$ reactions is facilitated, but along with this the effect of the substituent in *cis* and *trans* position is also attenuated, which substantially levels the difference between the two types of processes ($S_N1$ and $S_N2$) for these compounds. Confirmation of this is the poorly pronounced stereoselectivity of such pro-

cesses (see Table 2). The anomalously high concentration of the *cis* isomer in the case of phenylcyclopropane **4** at high current densities is probably due to the steric effect of the bulky phenyl group, which impede the approach of the molecule to the surface of the electrode on the side of the benzene ring.

As one switches from dibromocyclopropanes to dichlorocyclopropanes there is a sharp decrease of the reactivity of the latter, which is expressed in the higher cathode potentials for their reduction (see Table 1). In connection with the lower polarizability of the C−Cl bond, the possibility of the process following the $S_N1$ mechanism decreases sharply. The stereoselectivity of the reaction for this reason ceases to be dependent on current density, which is expressed by the identical *cis/trans* ratio for **7** in all cases (3.5:1).

The rate of the $S_N1$ reactions is dependent on experiment conditions. Therefore, confirmation of the proposed competing reduction of dihalocyclopropanes according to $S_N1$ and $S_N2$ mechanisms might be the change of ratio of *cis* and *trans* isomers as the conditions of electroreduction change for a constant current density, i.e., for a constant rate of the overall reaction. In this connection, the effect of the nature of the solvent and the background salt on the stereoselectivity of the process was investigated on the example of compound **5**, for which the effect of current density is manifested very distinctly. The results are given in Table 5. As can be seen, as one moves from less-polar ($CHCl_3$) to more-polar (DMF, DMSO), and then to protonic (MeOH) solvents, the *cis/trans* ratio decreases regularly in correspondence with the increase of the rate of the $S_N1$ reactions. A similar effect is seen when $Et_4NBr$ is replaced by $LiClO_4$, which is in agreement with the well-known accelerating effect of $LiClO_4$ on nucleophilic substitution reactions. Thus, the observed effect of the current density, the nature of the substituent, the solvent, and the background salt on the ratio of *cis*- to *trans*-monohalocyclopropanes is in agreement with the idea of competing electroreduction of the starting molecule according to the $S_N2$ mechanism and of ion pairs according to the $S_N1$ mechanism.

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