ORGANIC CHEMISTRY

SYNTHESIS BASED ON ELECTROGENERATED CARBENES.

COMMUNICATION 1. SOME REACTIONS WITH THE PARTICIPATION OF DICHLOROCARBENE

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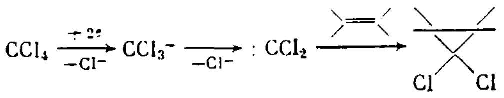
It can be concluded from the correlation of the scarce data on the electrolysis of CCl_4 in the presence of an organic substrate that the CCl_3^- anion, which is formed by the reduction of the C—Cl bond, either adds to an olefin, if the double bond is activated for nucleophilic addition [1], or fragments with the formation of dichlorocarbene (DCC) in media with low proton-donor properties. The DCC in its turn can [2] react with olefins, activated for electrophilic attack, forming derivatives of 1,1-dichlorocyclopropane. The existing information is, however, insufficient to determine the possibility of the synthetic utilization of the electrochemically generated DCC. With this purpose in mind, we accomplished the electrolysis of CCl_4 on a Pb cathode in the medium of $CHCl_3$ in the presence of different types of organic substrates (compounds with multiple C=C and C=N bonds, condensed aromatic systems, aromatic alcohols, and secondary amines).

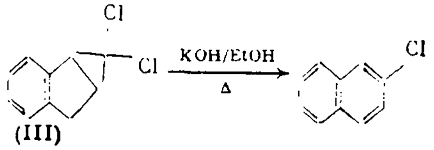
RESULTS AND DISCUSSION

The formation of the derivatives of 1,1-dichlorocyclopropane by the electrolysis of CCl_4 in the presence of an unsaturated organic substrate (Table 1, Expts. 1-5) can be described by the following scheme



The reproduction of the data of [2] for the isolation of 1,1-dichloro-2,2,3-trimethylcyclopropane (I) led to comparable results (Expt. 1). It seemed a principle to investigate the possibility of the reaction of the electrogenerated DCC with other olefins, having taken the described reactions of DCC, obtained by one or the other chemical method, as the basis. In this regard, cyclohexene is a convenient model. The electrolysis of CCl_4 on a Pb cathode in the presence of cyclohexene (Expt. 2) led to the formation of 7,7-dichloronorcarane (II), which was obtained by the electrolysis of CCl_4 on a Hg cathode with a somewhat lower yield [3].

The chemically generated DCC reacts with indene leading to different products depending on the reagents utilized. In our case (Expt. 3), the process proceeds analogously to [4] and leads to the 1,1-dichlorocyclopropane adduct (III) — a convenient starting material for the isolation of derivatives of 2-chloronaphthalene [4]. We utilized this reaction to confirm the structure of (III).



(III)

The reaction of DCC with aromatic substrates proceeds, as a rule, in a complex manner. For example, the reactions of DCC with condensed aromatic systems usually lead [5] to a mixture of unstable products. We only isolated 7,7-dichlorodibenzo[*a*, e]norcarane (IV) by the electrolysis of CCl_4 in the presence of phenanthrene (Expt. 4).

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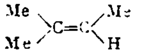
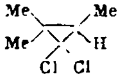
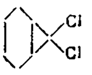
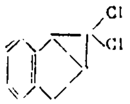
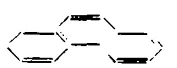
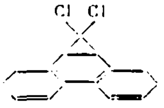
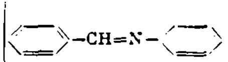
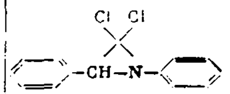
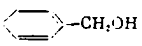
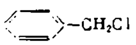
TABLE 1. Substance Yields (SY) and Current Yields (CY) of the Products of the Electrolysis of CCl_4 (C = 0.45-0.5 M) in the Presence of Substrates of Differing Nature (0.35 Alk_4NBr in $CHCl_3$) on a Pb Electrode

No. of expt.	Substrate	T, °C	Product	SY, %	CY, %	Conversion of substrate, %
1		-5	 (I)	–	66 *	–
2		-5	 (II)	86	45	15
3		0-5	 (III)	75	32	17
4		25	 (IV)	90	12.5	15
5		15-20	 (V)	80	19	25
6		27-28	 (VI)	83	36	22
7	Ph_2NH	20	Ph_2NCHO (VII)	95	58	26.6

*Literature data [2]; CY = 80%.

The introduction of dihalocarbenes at the C–H bond of an organic substrate can only usually be accomplished by the thermal method of the generation of the carbene species [5]. An attempt to introduce the electrogenerated DCC at the C–H bond of adamantane proved to be unsuccessful under the usual conditions at different temperatures. Further, we found that the electrogenerated DCC reacts with Schiff bases by undergoing addition at the C=N bond. Thus, 1,2-diphenyl-3,3-dichloroaziridine (V) was obtained from benzylideneaniline and DCC (Expt. 5).

Therefore, it can be concluded that the electrogenerated DCC reacts with the C=C and C=N multiple bonds forming the cycyclopropane and aziridine adducts.

The high selectivity of the process is brought to notice. In all cases, the reaction mixture only contains the requisite product, which is formed in an amount close to the degree of conversion of the substrate, apart from the unreacted organic substrate. Moreover, the cathode is passivated in the course of the electrolysis (after ~2-3 h); this is evidently one of the causes of the low (15-30%) conversion of the substrate and the moderate yields based on the current (20-66%).

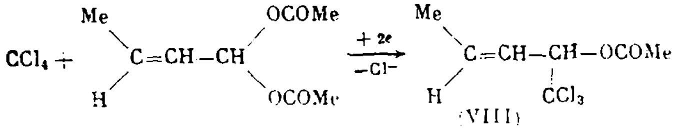
We also investigated the reactions of the electrogenerated DCC with alcohols and secondary amines. It was found that the generation of DCC in the presence of $PhCH_2OH$ (Expt. 6) leads to $PhCH_2Cl$ (VI). According to the data of [6], the mechanism of such a reaction includes the fragmentation of the ylide $R\overset{+}{O}(H)-\overset{-}{C}Cl_2$ which is formed as an intermediate. The reaction of DCC with secondary amines leads to disubstituted formamides [7-9]. The generally accepted mechanism of the process includes the formation of an ylide intermediate and its rearrangement with the subsequent stage of hydrolysis according to the scheme

$$R_2NH \xrightarrow{:CCl_2} R_2\overset{+}{N}H-\overset{-}{C}Cl_2 \rightarrow R_2N-CHCl_2 \xrightarrow{H_2O} R_2NCHO$$

However, this interpretation of the mechanism of the process should be treated cautiously since repeated attempts to identify the ylide or the product of its rearrangement in the absence of water (cf. e.g. [9]) were unsuccessful. By analogy, in the reaction of the electrogenerated DCC with diphenylamine (Expt. 7), the only reaction product separated proved to be Ph_2NCHO (VII) in spite of the precautions taken to exclude the presence of moisture in the reaction medium. Several products are formed by the electrolysis of CCl_4 in the presence of Et_2NH; diethylformamide is present among the products according to the data of the IR and NMR spectra.

The examples of the reaction of DCC, generated by one or the other chemical method, with different types of organic substrates were already described; these served as the main models for the accomplishment of the reactions, the results of which are summarized in Table 1. The results obtained in accordance with the data already known disclose the real promise of the utilization of the electrochemical method to accomplish the highly selective processes, under mild conditions, on the basis of reactions involving the electrogenerated DCC. However, it should be kept in mind that the problem of the optimization of the performance of such processes, associated with the selection of the electrode material, the medium, etc., has not been specifically investigated until now.

The analysis of the literature data showed that the nature of the added organic substrate changes during the electrolysis of CCl_4, and that it is possible to react the substrate with either DCC, as in the examples described (cf. also [2]), or the CCl_3^- anion if the added substrate possesses sufficiently strong electrophilic properties [1]. Our attention was drawn to the unusual reaction, described in [10], where the Makosza generation of DCC in the presence of the diacylal of an unsaturated aldehyde led to the formation of the product of the formal substitution of one of the acetate groups by the CCl_3^- anion, rather than the expected product of the cyclopropanation. These results are in complete conformity with the data obtained for our electrolysis of CCl_4 in the presence of the diacylal of crotonic aldehyde



(VIII)

The compound 1-acetoxy-1-trichloromethylbut-2-ene (VIII) was formed in practically a quantitative yield with the 17% conversion of the diacylal. The realization of such a process reveals the possibility of accomplishing the simultaneous cyclopropanation at the activated double bond and the trichloromethylation at the carbon atom connected to the acetate groups under the conditions of the electrolysis of CCl_4 with the selection of the corresponding substrate (cf. e.g., [10]).

EXPERIMENTAL

The electrolysis was performed with stirring in a glass vessel with a Teflon cover equipped with ceramic diaphragm with inlets for Ar, a thermometer, and a reflux condenser. The cathode was Pb-foil (50 cm^2); the anode was Pt (21 cm^2). The solutions of 0.35 M Bu_4NBr and Et_4NBr in $CHCl_3$ were utilized as background electrolytes. The working volume of the catholyte comprised 80 ml; the anolyte comprised ~40 ml. Cyclohexene was added to the anolyte for the absorption of Br_2. The electrolysis was conducted in a galvanostatic regime ($I \approx 0.15$-0.2 A) for 3-5 h in absolute solvents. All the liquid substrates were distilled under Ar; the solid substrates were recrystallized.

The GLC was performed on a "Chrom-5" instrument using a column of 2.4 m with NF SE-30 on Chromaton. The ^1H NMR spectra were taken on a "Tesla BS-497" instrument (60 MHz) in CCl_4 relative to HMDS. The TLC and column chromatography were performed using Silufol UV-254, silica gel LSL_{254} 5/40, and Al_2O_3-$L_{40/250}$ (neutr.) of the firm Chemapol.

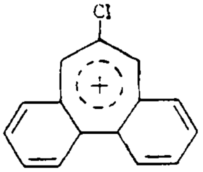
1,1-Dichloro-2,2,3-trimethylcyclopropane (I). The catholyte comprised 0.35 M Bu_4NBr, 3.5 ml (0.036 mole) of CCl_4, and 2.43 g (0.042 mole) of 2-methylbut-2-ene in $CHCl_3$. The anolyte comprised 0.35 M Bu_4NBr, 1.75 ml (0.018 mole) of CCl_4, and 4 ml (0.04 mole) of cyclohexene in $CHCl_3$. The transmission Q = 3088 C. A large part of the $CHCl_3$, the unconverted CCl_4, and 2-methylbut-2-ene were distilled from the catholyte on a water bath at atmospheric pressure. The remaining readily boiling substances were collected in a trap (cooled with a mixture of acetone and CO_2) with external warming to 100°C at p = 0.1 mm. After the distillation of $CHCl_3$, the distillation of the residue yielded 1.62 g of (I) (CY 66%) with the bp 55°C (30 mm) and the n_D^{20} 1.4560.

7,7-Dichloronorcarane (II). The catholyte comprised 0.35 M Bu_4NBr, 3.5 ml (0.036 mole) of CCl_4, and 5.8 ml (0.056 mole) of cyclohexene in $CHCl_3$. The anolyte comprised 0.35 M Bu_4NBr, 1.75 ml (0.018 mole) of CCl_4, and 4 ml of cyclohexene in $CHCl_3$. Q = 4630 C. A large part of the readily boiling substances was distilled from the catholyte at 40 mm into a trap; abs. hexane was added to the residue. The precipitated crystals of the background salt were filtered off and washed with hexane. After the distillation of the hexane, 1.2 g of (II) with the bp 78°C (15 mm) and the n_D^{23} 1.5014 (CY 45%, SY 86% for the 15% conversion) were obtained.

2,2-Dichloro-1,3-cyclotetralin (III). The catholyte comprised 0.35 M Bu_4NBr, 4.7 g (0.04 mole) of indene, and 3.6 ml (0.036 mole) of CCl_4 in $CHCl_3$. The anolyte comprised 0.35 M Bu_4NBr, 1.8 ml (0.018 mole) of CCl_4, and 4 ml (0.04 mole) of cyclohexene in $CHCl_3$. At the conclusion of the electrolysis (Q = 3070 C), the readily volatile substances were distilled into a trap at 20 mm; a large part of the indene (3.92 g) was distilled at p = 0.1 mm. The residue was passed through a column with Al_2O_3. The eluent was the 5:1 mixture of hexane–C_6H_6. After the evaporation of the solvent and traces of indene in vacuo, 1.0 g of (III) was obtained. The PMR spectrum was identical to that presented in [4]. The yields were CY 32% and SY 75% based on indene with the conversion of 17%.

The structure of (III) was confirmed by its conversion to 2-chloronaphthalene according to the method of [4]; it had the mp 57-59°C, cf. [11].

7,7-Dichlorodibenzo[*a*, e]norcarane (IV). The catholyte comprised 0.35 M Bu_4NBr, 2.5 g (0.014 mole) of phenanthrene, and 3.5 ml (0.036 mole) of CCl_4 in $CHCl_3$. The anolyte comprised 0.35 M Bu_4NBr, 1.75 ml (0.018 mole) of CCl_4, and 4 ml (0.04 mole) of cyclohexene in $CHCl_3$. At the conclusion of the electrolysis (Q = 3000 C), the readily boiling substances were distilled from the catholyte. The dry residue was extracted with hexane by the boiling and the subsequent decanting with 3 portions of 30 ml. The hexane was distilled in vacuo, and the residue was separated by the method of TLC on Silufol using the 10:1 mixture of hexane–ether. The following were isolated: 2.1 g of phenanthrene and 0.5 g of (IV) in the form of colorless crystals with the mp 140-140.5°C, cf. [12]. The yields were CY 12.5% and SY 90% based on the phenanthrene with the conversion of 15%. The structure of (IV) was confirmed by the comparison with a control sample obtained according to [13]. On the TLC using the 10:1 mixture of hexane–ether on Silufol, (IV) and the control sample are detected in UV light and have the same R_f. The spots on the plate acquire a blue color at $t > 140°C$; this is evidently associated with the known [12] conversion of (IV) to (IX).



(IX)

1,2-Diphenyl-3,3-dichloroaziridine (V). The catholyte comprised 0.35 M Et_4NBr, 1 g (0.005 mole) of benzylideneaniline, and 3.5 ml (0.035 mole) of CCl_4 in $CHCl_3$. The anolyte comprised 0.35 M Et_4NBr, 1.75 ml (0.018 mole) of CCl_4, and 4 ml (0.04 mole) of cyclohexene in $CHCl_3$. At the conclusion of the process (Q = 965 C), the mixture was treated by analogy with Expt. 2; 1.0 g of a dark yellow oil was isolated. According to the PMR data of the ratio of the integral intensities of the signals of the proton at 3.5 ppm in the aziridine and the proton at 8.25 ppm in the benzylideneaniline, it follows that the product of the electrolysis is the mixture of the initial compound and (V) (4:1 ratio); this corresponds with 0.745 g of the initial compound and 0.255 g of (V) (CY 19% and SY 80% based on the benzylideneaniline at the conversion of 25%). The TLC of the products of the electrolysis on Silufol in C_6H_6, in comparison with a control sample obtained according to [14], indicates that only the initial compound and (V) are present.

Benzyl Chloride (VI). The catholyte comprised 0.35 M Et_4NBr, 3 ml (0.029 mole) of $PhCH_2OH$, and 3 ml (0.03 mole) of CCl_4 in $CHCl_3$. The anolyte comprised 0.35 M Et_4NBr, 1.5 ml (0.015 mole) of CCl_4, and 3 ml (0.03 mole) of cyclohexene in $CHCl_3$. At the conclusion of the electrolysis (Q = 3412 C), 50 ml of H_2O was added to the catholyte; the aqueous layer was saturated with NaCl. After stirring the mixture, the organic layer was separated, and the aqueous layer was extracted with $CHCl_3$ (2 portions of 25 ml). The extract was dried over $CaCl_2$. The $CHCl_3$ was distilled. The distillation of the residue led to the isolation of 2.32 g of $PhCH_2OH$ with the bp 102°C (15 mm) and 0.8 g of (VI) with the bp 72-74°C (15-16 mm) (CY 36% and SY 83% based on $PhCH_2OH$ with the conversion of 22%).

Diphenylformamide (VII). The catholyte comprised 0.35 M Et_4NBr, 3.18 g (0.018 mole) of diphenylamine, and 3.5 ml (0.036 mole) of CCl_4 in $CHCl_3$. The anolyte comprised 0.35 M Et_4NBr, 1.75 ml (0.018 mole) of CCl_4, and 4 ml (0.04 mole) of cyclohexene in $CHCl_3$. Afer the electrolysis (Q = 1527 C), the readily boiling substances were distilled. Hexane was added to the residue; the residue was filtered off and washed with hexane. The filtrate was concentrated, and the residue was chromatographed on a column with silica gel. The first eluent was C_6H_6; 2.34 g of Ph_2NH were isolated. The second eluent was EtOH. After the evaporation of the EtOH, 0.91 g of (VII) with the mp 72°C was obtained. The structure of (VII) was confirmed by the PMR data. The yields were CY 58% and SY 95% based on Ph_2NH for the conversion of 26.6%.

1-Acetoxy-1-trichloromethylbut-2-ene (VIII). The catholyte comprised 0.35 M Bu_4NBr, 3.5 ml (0.036 mole) of CCl_4, and 2.1 g (0.009 mole) of crotonic aldehyde diacylal in $CHCl_3$. The anolyte comprised 0.35 M Bu_4NBr, 1.75 ml (0.018 mole) of CCl_4, and 4 ml (0.04 mole) of $CHCl_3$. At the conclusion of the electrolysis (Q = 2586 C), the readily volatile substances were distilled into a trap. Hexane was added to the residue. The precipitated salt was filtered off and washed with hexane. After the distillation of the hexane, the distillation of the residue led to the isolation of 2.22 g of a mixture with the bp 84°C (7 mm) consisting of the initial diacylal (79%) and (VIII) (21%) according to the GLC data; the control sample used for comparison was obtained according to [10]. This corresponded to 1.75 g of the initial reagent and 0.47 g of (VIII). The yields were CY 15% and SY 96% according to the GLC with the conversion of 17%.

CONCLUSIONS

The dichlorocarbene generated by the electrolysis of CCl_4 enters into reactions with organic substrates of varying nature under mild conditions and with high selectivity, the reactions are characteristic of dichlorocarbene.

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