SYNTHESIS BASED ON ELECTROGENERATED CARBENES. 3.

ELECTROCHEMICAL OXIDATION OF DINITROMETHYLIDES AS

A ROUTE TO GENERATION OF DINITROCARBENE

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We have previously discovered [1] the polarization curves (PC) of the electrooxidation of dinitromethylides (Ptanode, CH_3CN), the presence of one single quasidiffusional wave, the $E_{1/2}$ value of which is dependent on the structure of the ylide and varies in the range 1.7-2.0 V. In contrast with mononitromethylides [1], cation radicals (CR), formed during electrooxidation of dinitromethylides, undergo fragmentation at a rate greater than the reaction with the medium (splitting off of the H atom) and form an onium cation.

The data concerning the character of the fragmentation evoked particular interest since it is known that, photolysis or thermolysis of the ylides [2, 3] for example, leads to the formation of carbenes. Therefore, the main object of the present investigation was to study the process of electrochemical oxidation of sulfur and selenium dinitromethylides in greater detail than in [1].

The investigation was concentrated on the stable and readily available dimethylsulfonium dinitromethylide

 $Me_2S^+ - \overline{C}(NO_2)_2$ (I). In addition, sulfonium and selenonium dinitromethylides $Ph_2\overline{S} = \overline{C}(NO_2)_2$ (II), $S^- - \overline{C$

the patterns found. The experiments were carried out in absolute MeCN medium, containing $0.1N \text{ LiClO}_4$, on a Pt anode using the rotating disk electrode with ring (RDER) method and electrolysis carried out at a controlled potential.

RESULTS AND DISCUSSION

By carrying out the investigation using the RDER method, we found that during the oxidation of ylide (I) on a disk electrode (a wave with $E_{1/2} = 1.87$ V), in addition to the wave corresponding to the NO/NO⁺ redox pair ($E_{1/2} =$ 0.7 V), an anode wave with $E_{1/2} = 1.35$ V and cathode waves with $E_{1/2} = 0.3$; -0.5 and -0.8 V are found on the ring electrode (Fig. 1). These waves, like the NO/NO⁺ wave clearly correspond to processes with the participation of intermediates formed as a result of reactions initiated by the CR of ylide (I). Some of these intermediates (NO; an intermediate which is oxidized at $E_{1/2} = 1.35$ V) can be oxidized at the anode wave potentials of the ylide (I), which increases the height of this wave. Namely, the fact that the heights of the anode waves of the ylides and the coulometrically determined values of the numbers of electrons n, consumed at potentials of these waves, differ noticeably (for example, n = 1.2; 2.1 and $4\bar{e}$ for ylides (V), (I) and (IV) respectively), can be explained by the difference in the kinetics of the chemical stages included in the electrode process and leading to readily oxidizable intermediates. At the same time, the quasidiffusional character of the waves indicates that the chemical stages included in the electrode process proceed at very high but differing rates.

Further information on the characteristic features of the oxidation of the ylide (I) was obtained by studying the dependences of the current efficiency on the ring electrode N_r of the anode waves with $E_{1/2} = 0.7$ and 1.35 V on the rotation velocity m and potential of the disk electrode E_d . Of particular significance, it could be seen that during the

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Fig. 1. Polarization curves of dimethylsulfonium dinitromethylide (C = $8 \cdot 10^{-3}$ mole/liter), recorded on a ring electrode in CH₃CN on the background of 0.2 N LiClO₄: 1) at a disk electrode potential of E_d = 1.8 V; 2) without polarization of the disk electrode (m = 1800 rpm).



Fig. 2. Dependence of the current yield on the ring electrode on the disk electrode potential (m = 1800 rpm (a)) and on the rotation velocity of the electrode ($E_d = 1.8$ V) (b); 1) NO⁺; 2) NO; 3) compound with $E_{1/2} = 1.35$ V.

oxidation of (I) on the disk electrode, the particles with $E_{1/2} = 1.35$ and 0.7 V, recorded on the ring electrode, enter into further electrochemical or chemical transformations, which complicates the mechanism of the oxidation of (I). In fact, the values of N_r for the above particles decrease when E_d is shifted to more anodic potentials along the oxidation wave of (I) (Fig. 2a).

For the cathode and anode branches of the reversible wave with $E_{1/2} = 0.7$ V, the $N_r = f(\sqrt{m})$ dependence decreases with increase in m (Fig. 2b, curves 1 and 2). This means [4] that the slowest stage is that of formation of NO.^{*} Hence, NO cannot be formed directly from the CR of (I), and in addition to the primary event of the decomposition of CR, this process also includes several stages.

For the wave with $E_{1/2} = 1.35$ V, the $N_r = f(\sqrt{m})$ dependence increases with increase in m (Fig. 2b, curve 3). Hence, for the intermediate oxidized at these potentials, the slowest stage is that of its chemical transformations. The particle itself should be relatively stable, since its oxidation wave is recordable even at low (600 rpm) rotation velocities of the electrode. We found that, according to the potential, the wave with $E_{1/2} = 1.35$ V exactly coincides with the oxidation wave of Me₂S. This fact is surprising. It was found that during the oxidation of, for example, ylides (II) and (III) on a disk electrode, oxidation waves with $E_{1/2} = 1.16$ and 1.30 V are obtained on the ring electrode, which have the same potentials as the oxidation waves of Ph₂S and tetrahydrothiophene, respectively. These data confirm the veracity of the conclusion that the stable particle found on the ring electrode (the wave with $E_{1/2} = 1.35$ V) is Me₂S

^{*}The NO⁺ particle is clearly formed electrochemically because some of the NO molecules can be oxidized on the disk electrode.

itself. It is significant that Me₂S like the NO intermediate (see above) cannot be the product of a direct decomposition of the CR of (I) at the S-C bond, but is probably formed in a more complex way.^{*} Finally, during the oxidation of Me₂S on a disk electrode the same cathode waves are obtained ($E_{1/2} = -0.5$ and -0.8 V, see above) as during the oxidation of (I).

On the other hand, in the electrolysis products of (I) at a potential on a plateau of its oxidation wave (E = 2.0 V), compounds were detected by the TLC, GLC and UV spectroscopy which contain a dinitromethyl fragment $[C1HC(NO_2)_2 \text{ and } C1_2C(NO_2)_2]$ in an overall yield of >20%. The results obtained indicate that the cleavage of the bonds during an electrooxidation of (I) occurs in such a way that both the sulfide and dinitromethyl fragments of the molecules are retained. With this fact considered, and on the basis of the above direct and indirect data, the electrooxidation process can be represented by a scheme including a limited number of reaction paths, from which a choice is made

Scheme 1 $Me_{2}\overset{\cdot}{S} - \overline{C}(NO_{2})_{2} \xrightarrow{(a)} Me_{2}S + \overrightarrow{C}(NO_{2})_{2} \xrightarrow{fragmentation} NO, N\overset{\cdot}{O} \text{ etc.}$ $Me_{2}\overset{\cdot}{S} - \overrightarrow{C}(NO_{2})_{2} \xrightarrow{(b)} Me_{2}\overset{\cdot}{S} + \overrightarrow{C}(NO_{2})_{2} \xrightarrow{(cIO_{4}^{-})} HCCl(NO_{2})_{2}, \xrightarrow{(cI_{2}C}(NO_{2})_{2}, \xrightarrow{(cI_{2}C}(NO_{2})_{2})} \xrightarrow{(cIO_{4}^{-})} HCCl(NO_{2})_{2}, \xrightarrow{(cIO_{4}^{-})} HCCl(NO_{4}^{-}) \xrightarrow{(cIO_{4}^{-})} HCCCl(NO_{4}^{-}) \xrightarrow{(cIO_{4}^{-})} HCCCL(NO_$

The CR of (I) was in fact found to be very unstable particle. The peak of its reduction is absent on the inverse branch of the cyclic voltamperogram even at a scanning velocity of the potential equal to 500 V/sec. This makes it possible to evaluate the lifetime of the CR as $\leq 5 \cdot 10^{-4}$ sec.

The fragmentation of the CR by path (a) clearly cannot be realized. For example, it is not very probable that energetically unfavorable α -nitrocationoid particles will be formed (cf. [5]). Moreover, the possibility of the formation of Me₂S directly during the cleavage of the S-C_{NO2} bond of the CR has already been discussed above and discounted.

Attention should be also paid to path (c) with the formation of the dication $(CH_3)_2S^{++}$, since this cation cannot be oxidized under the experimental conditions at the 1.35 V potential (the wave recorded on the ring electrode) nor be converted into Me₂S. On the other hand, anion-radical $C(NO_2)_2^-$ should be immediately oxidized to $:C(NO_2)_2$ (this corresponds to case (b)). In any case, neither dinitromethane nor its anion were detected, even in trace amounts, as possible products of the reaction of the intermediate $C(NO_2)_2^-$ with the medium acidified during the electrolysis of (I) (see below).

The most probable is path (b) leading to the generation of dinitrocarbone (DNC). Incidentally, we should note that ylides are often considered to be potential sources of generation of carbene [2, 3]. In this case, the presence of $ClCH(NO_2)_2$ and $Cl_2C(NO_2)_2$ in the electrolysis products of (I) is the result of the reaction of DNC with the CIO_4^- anion. The presence of the wave of the NO/NO⁺ redox pair on the polarization curves recorded during the electrolysis of (I) means that the DNC formed may both react with the perchlorate ion and decompose to nitrogen oxides (Scheme 1(b)). These conclusions agree with the above results obtained in the investigation by the RDER method. If we assume that the chlorine derivatives of dinitromethane are formed in the reaction of DNC with the CIO_4^- ion as primary products of the fragmentation of the ylide CR, then the sulfide residue should in this case be a Me₂S CR (Scheme 1b). From this standpoint, we can explain some of the experimental data. In accordance with Scheme (2), the Me₂S CR can be deprotonated [6] and be further oxidized to the $CH_3 - \tilde{S} = CH_2$ cation (route 2(b)) or similarly to the CR of mononitromethylides [1], trialkylamines [7, 8] and certain other CR, can reaction with the medium with splitting off of the H atom

Scheme 2

 $Me_2S \xrightarrow{-e} Me_2S \xrightarrow{-e} Me_2S \xrightarrow{(a)} Me_2SH \longrightarrow Me_2S + H^+$ $(b) \longrightarrow Me \xrightarrow{+} S = CH_2 \longrightarrow Chemical reaction products in the bulk [6]$

The thus formed $(CH_3)_2 \overset{\circ}{S}H$ cation has a high acidity $(pK_a^{H_2O} = -5.2[9])$ and during the dissociation gives Me_2S (Scheme 2a). The Me₂S CR most probably reacts by the two above paths. In this case, the oxidation of the medium

^{*}The oxidation potential of (I) is ~500 mV more positive than the oxidation potential of Me₂S; the latter, during its formation directly from the CR of (I), whose fragmentation proceeds at a high rate, should immediately enter into an electrode reaction on the disk, and the wave with $E_{1/2} = 1.35$ V would not be obtained on the ring electrode.

during the electrolysis of the ylide (Scheme 2), the low value of $N_r(2-5\%)$ for the anode wave of Me_2S ($E_{1/2} = 1.35$ V), and the mechanism of the indirect (see above) formation of this compound, become understandable. The increase in the acidity of the medium during the electrolysis of (I) may be confirmed experimentally by the appearance and increase with time of the cathode wave with $E_{1/2} = -0.5$ V. The same wave corresponding to the reduction of H⁺ or protonation of the complex, is obtained on the ring electrode during the oxidation on the disk of both (I) and Me₂S. The wave with $E_{1/2} = -0.5$ V was identified by comparison with the cathode wave of discharge of H⁺ formed from HClO₄, which in CH₂CN is completely dissociated.

Thus, all the direct and indirect data obtained by the voltamperometry and electrolysis methods at a controlled potential during the investigation of the anodic behavior of (I) indicate that the generation of DNC in the course of this process can be considered as fully reliable.

The electrochemical behavior of dinitromethylides of various structures in general follow the same patterns. Some differences in the electrochemical behavior of dinitromethylides (I)-(V) are due only to the influence of substituents at the heteroatom. Thus, for example, compound (II) is oxidized with considerably greater difficulty than (I) and (III), which indicates that in the sulfonium compounds, the phenyl substituents display a clearly pronounced I-effect. However, the most characteristic is the fact that the electrooxidation of the dinitromethylides studied proceeds with the cleavage of the bond between the heteratom and the C atom of the nitrocarbanion group and retention of the dinitromethyl group. This is confirmed by the detection of chloro derivatives of dinitromethane in the electrolysis products of (I)-(V), and also finding of derivatives of the heteroatomic fragment of the ylide on the ring electrode (see above).

EXPERIMENTAL

The voltamperometric measurements and electrolyses were carried out in a glass cell thermostated at $25 \pm 0.1^{\circ}$ C with the cathode and anode spaces separated by a glass filter. The temperature was maintained by a U-1 ultrathermostat. The volume of the anolyte was 15-30 cm³. The polarization curves were recorded on a rotating platinum disk electrode (S = $7.61 \cdot 10^{-3}$ cm²) by means of a P-5827 M potentiostat.

To carry out the electrolyses, a platinum disk electrode with a ring of special construction was used at an electrode rotation velocity of m = 1800 rpm. A disk electrode with $S = 8.3 \cdot 10^{-3}$ cm² served as an indicator electrode, while the electrolysis itself was carried out on the ring electrode with S = 2 cm².

In the investigations using the rotating disk electrode with a ring, an electrode with the following characteristics was used: $S_d = 0.239 \text{ cm}^2$, $S_r = 0.261 \text{ cm}^2$ and N = 0.442. The potential on the disk electrode was applied by means of a potentiostat designed at the institute of Organic Chemistry of the Academy of Sciences of the USSR ($U_{output} = 50 \text{ V}$, $I_{output} 0.5 \text{ A}$) and was controlled by a Shch-1513 digital voltmeter. The polarization curves on the ring electrode were measured by means of a P-5827 M potentiostat.

The cyclic voltamperograms were recorded on a S8-11 screen persistent oscillograph using a rapid action PB-500 potentiostat, and a platinum disk electrode (S = $7.61 \cdot 10^{-3}$ cm² in a stationary state.

All the experiments were carried out in absolute MeCN on a background of 0.1-0.2 N LiClO₄, using Ag/0.1 N Ag⁺ in MeCN as reference electrode, and the values of the potentials are given relative to this reference electrode. The working concentrations of the depolarizer in the voltamperometric measurements were $1\cdot10^{-3}-8.10^{-3}$ mole/liter, and in carrying out the electrolysis $-1\cdot10^{-2}-5.10^{-2}$ mole/liter.

Chloro- and dichlorodinitromethane were identified by comparison with authentic samples, obtained according to [10] and their quantitative determination was carried out by GLC on a LKhM-8MD chromatograph at 90-150°C on a 70 m \times 0.25 mm glass capilary with an OV-17 phase. Flame ionization detector, carrier gas He. The change in the concentration of the ylides during the electrolysis was monitored spectrophotometrically on a Specord UV-VIS apparatus, using λ_{max} (nm) and ε equal for (I) to 329 and 9450, (II) – 324 and 6800; (III) – 331 and 10700, (IV) – 346 and 7900, (V) – 339 and 7300, respectively.

Acetonitrile was dehydrated by 5-7 times repeated distillation over P_2O_5 with subsequent distillation without the drying agent. Dinitromethylides (I) and (II) were obtained according to [11], (III)-(IV) according to [12].

CONCLUSIONS

The electrochemical oxidation of S and Se dinitromethylides on a Pt anode in absolute MeCN is accompanied by the fragmentation of the molecule at the heteratom—ylide C atom bond with the proabable formation of dinitrocarbene.

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ELECTROCHEMICAL CHLORINATION OF MONOTERPENE

OLIGOOLEFINS

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One of the methods for the selective functionalization of the terminal trisubstituted C=C bond of linear isoprenoid oligoofelins consists in their allytic chlorination by hypochlorites [1-3], sulfuryl chloride [4], sulfoxide hydrochlorides [5] and other reagents [6-8], differing in their effectiveness and availability. In this connection the method of electrochemical chlorination of monoterpene oligoolefins can be of positive interest.

The first attempts to carry out an electrochemical preparation of allyl chlorides in homogeneous aqueous mixtures showed [9, 10] that this process is complicated by the formation of chlorohydrins. The use of a heterogeneous aqueous—organic mixture [10] was found to be more effective, but the patterns of this process are still not sufficiently clear. The object of the present work was to clarify this problem, and also to develop an electrochemical method of preparation of allyl chlorides from olefins (Ia-e).

The electrochemical chlorination was carried out in a diaphragmless electrolyzer in a NaCl- CH_2Cl_2 system. Thus, instead of the Pt anode (cf. [9, 10]), a ruthenium oxide-titanium anode (ROTA) was used, which has gained wide acceptance in processes of electrochemical separation of chlorine.

RESULTS AND DISCUSSION

The electrolysis on ROTA of a well emulsified aqueous solution of NaCl and a solution of monoterpenes (Iae) in CH_2Cl_2 produces (Table 1) the corresponding methallyl chlorides (IIa-e)^{*}

*Usually the hydrolysis concluded after the practically complete conversion of the initial compound (the TLC data); a more prolonged electrolysis led to a mixture of mono- (II) and dichloro derivatives. The latter (during the electrochlorination of (Ia-d)) had the structure of (II') according to the PMR data.

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