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Electrochemical methods for the generation of carbenes and their analogues

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ABSTRACT. The present review surveys and analyses the results of studies devoted to the use of electrochemical methods for the generation of carbenes, nitrenes, and also dichlorogermylene. The cathodic and anodic processes leading to the formation of these species are considered separately. Attention is concentrated on questions concerning the generation of dihalogenocarbenes in the cathodic reduction of polyhalogenomethanes and of dinitrocarbene in the anodic oxidation of dinitromethylides. In addition, data are presented concerning the possibility of the cathodic generation of carbene and nitrene radical-anions and the study of their properties. The examples of reactions involving electrochemically generated carbenes and their analogues examined in the review indicate that there are realistic prospects for the creation of highly selective processes leading to the electrochemical carbene synthesis.

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I. Introduction

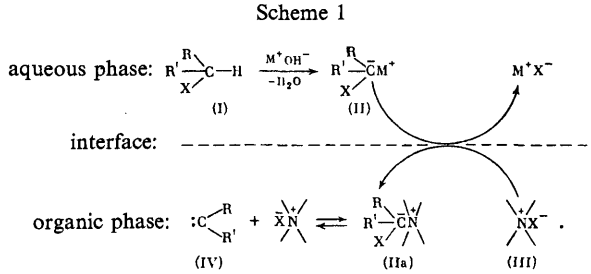
The various methods for the generation of carbenes are based on a fragmentation process initiated as a rule by the application of some kind of method involving a physical influence on a suitable organic substrate. Fragmentation results in the synchronous or successive dissociation of all the chemical bonds belonging to one reaction centre of the substrate molecule.

The aim of the present review is to show that, together with common methods for exerting a chemical influence such as, for example, thermolysis or photolysis, the electrochemical method can be used successfully for the generation of carbenes. In the last case, the fragmentation of the organic substrate leading to the formation of a carbene becomes possible because of the electrochemical activation of the substrate as a result of the transfer of one or several electrons. Such activation can be achieved as a result of the occurrence of both cathodic and anodic processes depending on the nature and structure of the substrate. Generally speaking, the method for the electrochemical generation of carbenes and their analogues has not yet come to be widely used and this review is perhaps the first attempt at a survey of the available experimental data. Nevertheless the many advantages of this method give rise to confidence that it has good prospects.

II. Reduction processes

One of the commonest methods of generating carbenes is the α-elimination of a substituent (usually a halide ion) from the carbanionic centre of a thermodynamically unstable anion. The conditions for the formation of such an anion exert a decisive influence on the efficiency of the generation of the carbene as a whole. Nowadays the greatest popularity has been gained by Makosha's method,[1] which is based on the following processes presented in Scheme 1:

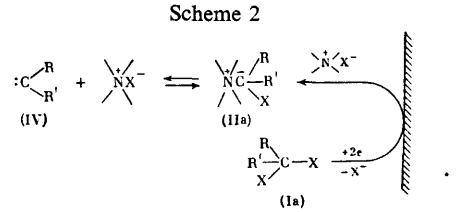
Scheme 1



The thermodynamically unstable carbanion (II) [zwitter-ion?] generated in the aqueous phase exchanges at the interface the metal cation for the tetraalkylammonium cation of the corresponding salt (III), catalytic amounts of which are added to the organic phase. The ion pair (IIa) formed migrates into the bulk of the organic phase where it dissociates with formation of the carbene (IV).

An alternative electrochemical method of generating the ion pair (IIa) does not require the presence of a base in the system and involves the reduction at the cathode of the C–X (X = halogen) bond of the precursor: †

Scheme 2



† In the light of the results of recent studies,[2] the following process occurs under certain conditions:

$$\rangle C{-}H + e \rightarrow \rangle C^{-} + {}^{1}/_{2}H_{2}.$$

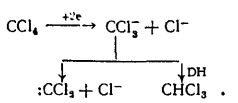
This is yet another possibility, in principle, of an effective electrochemical generation of a thermodynamically unstable carbanion and later a carbene. This possibility is being investigated at the present time.

Despite the fact that the process illustrated in Scheme 2 is evidently attractive, it would be premature to speak of its advantages over the thoroughly investigated process shown in Scheme 1. There is no doubt that the development of research into the electrochemical generation of carbenes (Scheme 2) has aroused interest both as regards the solution of specific synthetic problems and as a source of additional information about the mechanism of the process illustrated in Scheme 1.

1. Generation of carbenes

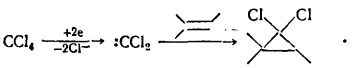
The possibility, in principle, of carrying out Scheme 2 was demonstrated as early as the beginning of the 1960's by Wawsonek and Duty,[3] who used the method of classical polarography to investigate the electrochemical reduction of various halogenomethanes in acetonitrile (AN) and dimethylformamide (DMF) and established that two electrons are transferred in the first stage [$E_{1/2}$ = –0.25 V (saturated calomel electrode)] of the reduction of CCl_4 at a Hg cathode in AN in the presence of Bu_4NBr as the supporting electrolyte. It is accompanied by the dissociation of the C–Cl bond and the formation of the carbanion CCl_3^-, which is partly protonated under the experimental conditions, affording $CHCl_3$, and undergoes partial fragmentation, which leads to the dichlorocarbene and Cl^-:

Scheme 3



The relative contributions of the above reactions depend on the proton-donating capacity of the medium. In the presence of proton donors (for example, H_2O), $CHCl_3$ is formed preferentially. The dichlorocarbene generated via Scheme 3 has been detected chemically by trapping it with an alkene (the yield of the adduct has not been indicated):[3]

Scheme 4



This process has been achieved at a Hg cathode in AN in the presence of Bu_4NBr as a supporting electrolyte at 20 °C and a current density of $(4 - 7) \times 10^{-3}$ A cm^{-2}. In view of the identity of the polarographic behaviour of CBr_4 and CCl_4, the same workers[3] concluded that dibromocarbene is probably formed on reduction of CBr_4. In addition, it has been suggested[3] that the reduction of CF_2Cl_2 and $PhCCl_3$ leads to difluoro- and phenylchloro-carbenes respectively. However, the formation of these carbenes has not been confirmed chemically.

Almost 20 years were needed before the conversion of alkenes into cyclopropanes in the electrochemical reduction of halogenomethanes was brought to the preparative level.[4–6] The successful solution of this problem was promoted by the rational selection of the electrode material and the solvent. Thus the current yield of cyclopropanes reaches 80% in the reduction of CCl_4 at a lead electrode in $CHCl_3$ in the presence of alkenes (Table 1, experiments 1–4).[4]

According to the authors,[4] the following processes can also lead to the formation of dichlorocarbene in the electrolysis of CCl_4 in $CHCl_3$ under these conditions:

Scheme 5

$$CHCl_3 + 2e \rightarrow CHCl_2^- + Cl^-,$$
$$CHCl_3 + CHCl_2^- \rightarrow CCl_3^- + CH_2Cl_2,$$
$$CCl_3^- \rightarrow :CCl_2 + Cl^-.$$

Table 1. The electrolysis conditions and the yields of the products of the conversion of alkenes into cyclopropanes by electrochemically generated dihalogenocarbenes.

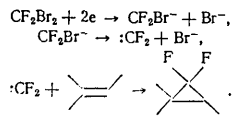
No. of expt.	Initial halogeno-methane	Carbene formed	T, °C	Solvent	Bu_4NBr concentration, M	Electrode	j, mA cm^{-2}	Alkene employed	Yield* of cyclopro-pane	Refs.
1	CCl_4	$:CCl_2$	—5÷—3	$CHCl_3$	0.35	Pb	2.5	2-methylbut-2-ene	80—82	[4]
2	CCl_4	$:CCl_2$	—5÷—3	$CHCl_3$	0.35	Pb	4.0	styrene	56—58	[4]
3	CCl_4	$:CCl_2$	—5÷—3	$CHCl_3$	0.35	Pb	2.5	2-phenylpropene	65—67	[4]
4	CCl_4	$:CCl_2$	—5÷—3	$CHCl_3$	0.35	Pb	4.0	2,3-dimethylbut-2-ene	77—82	[4]
5	CCl_4	$:CCl_2$	—5÷—3	CH_2Cl_2	0.25	Pb	4.0	2-methylbut-2-ene	62—63	[4]
6	CF_2Br_2	$:CF_2$	0÷18	CH_2Cl_2	0.35	Pt	1.0	2-methylbut-2-ene	54	[5]
7	CF_2Br_2	$:CF_2$	0÷18	CH_2Cl_2	0.35	Pt	1—2	2-phenylpropene	48—57	[5]
8	$CFBr_3$	$:CFBr$	<0	CH_2Cl_2	0.25—0.35	Pb	1—2	2-methylout-2-ene	~60	[6]
9	$CFBr_3$	$:CFBr$	<0	CH_2Cl_2	0.25—0.35	Pb	1—2	styrene	~60	[6]
10	$CFBr_3$	$:CFBr$	<0	CH_2Cl_2	0.25—0.35	Pb	1—2	cyclohexene	~60	[6]

* Calculated relative to the product isolated.

Indeed the electrolysis of $CHCl_3$ itself in the presence of 2-methylbut-2-ene afforded *gem*-dichlorocyclopropane in 22–25% yield.[4] Dichlorocarbene can be generated from CCl_4 also in CH_2Cl_2 whose acidity is insufficient for the protonation of CCl_3^-. The yield of cyclopropanes from alkenes proved to be fairly high also under these conditions (Table 1, experiment 5).

The reduction of CF_2Br_2 at a platinum cathode in CH_2Cl_2 leads to $:CF_2$, which interacts with 2-phenylpropene or 2-methylbut-2-ene to form difluorocyclopropane derivatives in good yields (Table 1, experiments 6 and 7):[5]

Scheme 6



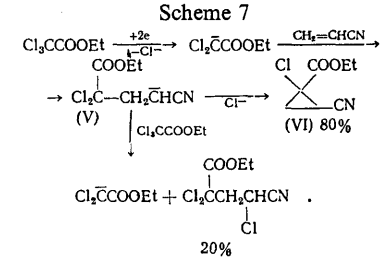
The reduction of $CFBr_3$ takes place similarly at a lead cathode. It leads to :CFBr, which forms bromofluorocyclopropane derivatives in the presence of alkenes (Table 1, experiments 8–10).[6]

We may note that the (IIa) → (IV) reaction stage presented in Schemes 1 and 2 provides an incomplete idea about the reactivity of the intermediate anion (IIa). In reality, this anion is capable of being partly protonated even in aprotic media of the type of AN, DMF, and propylene carbonate[5] (see Scheme 3). The polarisation curves for the reduction of CCl_4 then show a wave (the second wave) corresponding to the reduction of $CHCl_3$. It is of interest that the height of the second wave depends on the presence in the solution of an alkene, which functions as an acceptor of carbenes.[7] In certain cases, such data can serve as indirect confirmation of the formation of the carbene intermediate.[7]

The protonation of the anion (IIa) can influence greatly the efficiency of the generation of the carbene. For example, whereas the rapid proton exchange reactions between $CHCl_3$ and the electrochemically generated anion CCl_3^- do not lower the yield of dichlorocarbene on reduction of CCl_4 in chloroform because they lead to the same readily fragmented anion CCl_3^-,[4] the reduction of CF_2Br_2 in chloroform affords F_2CH_2. Owing to the high basicity of the intermediate anion CF_2Br^-, it is better to generate $:CF_2$ in the latter case in the less acid CH_2Cl_2.[5] In the generation of the highly basic anions (IIa) (see Scheme 2) in a medium containing the cations NR_4^+ (R = alkyl), account must be taken of the possibility of the Hofmann cleavage of the cations (for R ≠ Me) with formation of alkenes under the influence of compound (IIa) as a base.

In media with weak proton-donating properties, the carbene formed on fragmentation of the intermediate anion (IIa) interacts with alkenes, as shown in Schemes 4 and 6. However, when the double bond has been activated in relation to nucleophilic attack, the anion (IIa) can react rapidly with the alkene and the stage (IIa) → (IV) (see Scheme 2) is then excluded. This possibility has in fact been examined in detail by Baizer and Chruma[8] [including the process involving the anion CCl_3^- generated by the electrochemical reduction of CCl_4 at a mercury cathode in DMF in the presence of NEt_4Cl as the supporting electrolyte at an electrolysis potential of –0.85 V (w.r.t. sat. calomel electrode) and at a temperature of 25–45 °C]. It must be emphasised that, together with the products of the addition of the carbanion to the double bond, cyclopropane derivatives can also be formed in this case, as happens, for example, in the reduction of trichloroethyl acetate in the presence of acrylonitrile[8] (Scheme 7):

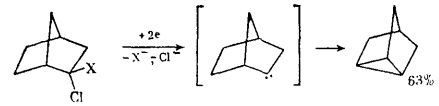
Scheme 7



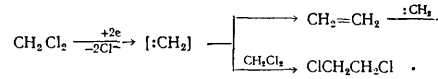
It is significant that cyclopropane (VI) is formed exclusively as a result of the intramolecular cyclisation of the adduct of the carbanion with the alkene (V).[8]

The data examined above are extremely important for the selection of optimal conditions for the synthesis of cyclopropanes with participation of electrochemically generated carbenes.

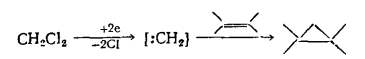
The electrochemical reduction of organohalogen compounds in accordance with Scheme 2 can be used to generate not only halogenocarbenes but also carbenes with a different structure. Thus, in the reduction of 2,2-dichloronorbornane [$E_{1/2}$ = –1.54 V (sat. c. e.)] or 2-bromo-2-chloronorbornane [$E_{1/2}$ = –0.83 V (sat. c. e.)] at a mercury cathode in DMF in the presence of NEt_4Br as the supporting electrolyte, the intermediate carbene is inserted in a C–H bond, which leads to a high yield of an intramolecular cyclisation product:[9]



According to Mottus and Ort,[10] the electrolysis of a CH_2Cl_2 solution containing $AlCl_3$ at an aluminium cathode leads to dichloroethane, ethylene, and cyclopropane (the yields have not been indicated), which are regarded as the methylene conversion products:

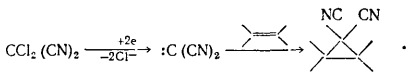


The reduction of different halogenomethanes by the electrochemically generated solvated electrons [aluminium cathode coated with lithium and magnesium in solution in hexamethylphosphoramide (HMP) containing LiCl and $MgCl_2$] leads to a mixture of gases (ethane, ethylene, cyclopropane, etc.), whose formation is explained by the participation of methylene.[11] In the presence of an alkene, the corresponding cyclopropanes were obtained:



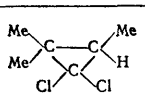
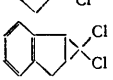
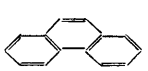
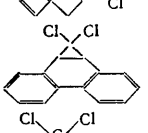
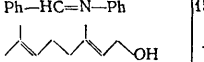
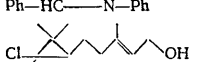
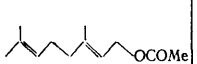
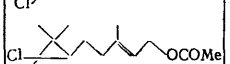
It has been shown by the polarographic method[12] that the carbene intermediate is formed also in the electrochemical reduction of 9,9-dichlorofluorene. Similarly, dicyanocarbene is formed as an intermediate in the reduction of dichloromalononitrile.[13] The results of polarographic studies and of electrolysis at a controlled potential [E = –0.47 V (rel. Ag/Ag^+), Hg cathode, AN, NBu_4Br,

0–5 °C] in the presence of tetramethylethylene made it possible to describe this process by the following scheme:



However, the yield of the cyclopropane proved to be less than 1%.

Table 2. The material and current yields of the products of the electrolysis of CCl_4 (c = 0.5 M) in $CHCl_3$ in the presence of various organic substrates.

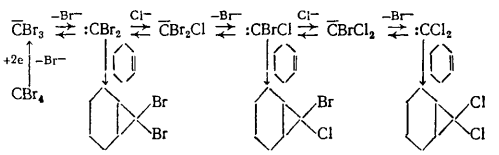
No. of expt.	Substrate	T, °C	Product	Yield, % w.r.t. material	Yield, % w.r.t. current	Refs.
1	$Me_2C{=}CHMe$	—5		—	66*	[14]
2		—5		90	45	[14]
3		0—5		75	32	[14]
4		25		90	12.5	[14]
5	Ph—HC=N—Ph	15—20	Ph—HC—N—Ph	80	19	[14]
6		—5		26	13	[15]
7		20		61	32	[15]
8	$PhCH_2OH$	27—28	$PhCH_2Cl$	83	36	[14]
9	Ph_2NH	20	Ph_2NCHO	95	58	[14]

Note. The electrochemical reduction was carried out at a lead cathode at j = 2–4 mA cm^{-2} in the presence of 0.35 M NR_4Br (R = alkyl) as the supporting electrolyte.
* According to Fritz and Kornrumpf,[4] the yield is 80%.

After the studies which confirmed the carbene mechanism of the processes considered above, it was important to assess the possibility of the synthetic application of the electrochemically generated carbenes. In particular, studies[14,15] on the electrolysis of CCl_4 at a lead cathode in $CHCl_3$ in the presence of organic substrates of different nature have shown that the dichlorocarbene generated in this way is capable of interacting under mild conditions with the C=C and C=N double bonds, forming cyclopropane and aziridine adducts (Table 2). According to the mechanism adopted,[16,19] the interactions with an alcohol and an amine (Table 2, experiments 8 and 9) proceed via the intermediate formation of ylide structures and lead to benzyl chloride and diphenylformamide respectively.

Dichlorocarbene reacts selectively with geraniol and geranyl acetate (Table 2, experiments 6 and 7) at the terminal double bond. The above reactions are highly selective. Cathodic electrolysis (lead cathode, j = 1–3 mA cm^{-2}) of CBr_4 in the presence of NBu_4BF_4 as the supporting electrolyte in cyclohexene-containing AN leads to the exclusive formation of 7,7-dibromonorcarane,[20] while the electrolysis of CBr_4 in CH_2Cl_2 in the presence of benzyltriethylammonium chloride as the supporting electrolyte results in a mixture of 7,7-dibromo, 7-bromo-7-chloro-, and 7,7-dichloro-norcaranes in an overall yield up to 85%. A number of reactions, inititated by the interaction of the electrochemically generated dibromocarbene with a chloride ion, take place during the electrolysis:[20]

Scheme 8



By varying the nature of the supporting electrolyte, it is possible to obtain predominantly (up to 65%) a particular dihalogeno-derivative (Scheme 8) as a mixture with other dihalogeno-derivatives obtained in an overall yield of ~80%.

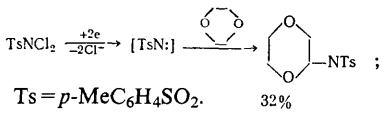
The examples considered above reveal good prospects for the creation of electrochemical processes for carbene synthesis, which may compete with traditional methods. It follows from the analysis of literature data that the formation of cyclopropane derivatives in high yields is promoted by carrying out the process at a relatively low current density (j = 1–5 mA cm^{-2}), a high alkene concentration relative to the source of the carbene, the use of halogenomethanes as solvents, and the use of tetraalkylammonium halides as supporting electrolyte salts, the readily soluble tetrabutylammonium salts being preferable. Furthermore, the replacement of NBu_4Br in the electrochemical synthesis of difluorocarbene from CF_2Br_2, for example, by NEt_4Br, promotes faster formation of a passivating layer of polytetrafluoroethylene on the electrode.[5] (We may note, however, that the question of the passivation of the electrode as well as the main causes of the low degree of conversion of the organic substrate has still been little investigated.)

2. Generation of carbene analogues

Nitrenes. The electrochemical reduction of organohalogen compounds makes it possible to generate also a nitrene, which is an important reaction intermediate.

On the basis of the results of preparative electrolysis in galvanostatic and potentiostatic regimes, the possibility of generating nitrenes from the corresponding *NN*-dichloro-derivatives at different electrodes (Pt, Zn, Cu, Hg, and C) has been demonstrated.[21–23] The electrochemical reduction of *NN*-dichloro-derivatives of toluene-*o*- and toluene-*p*-sulphonamides in the range of potentials 0.30–0.35 V takes place with transfer of two electrons.[21–23] As a result, the N–X (X = halogen) bond is ruptured in the first stage, as in the reduction of polyhalogenoalkanes. The fragmentation of the N-anion formed under these conditions (cf. Scheme 2) leads to a nitrene. Indeed, the electrochemical reduction of *NN*-dichlorosulphonamides at a platinum cathode in AN in the presence of $LiClO_4$ as the supporting electrolyte and 1,4-dioxane, with which nitrenes react,[24]

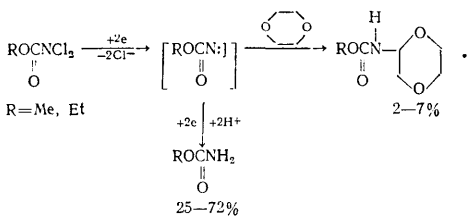
affording the products of insertion in a C–H bond, led to the formation of the corresponding adduct:



Ts = *p*-$MeC_6H_4SO_2$. 32%

Nitrenes can be generated similarly also in the cathodic reduction of *NN*-dichlorocarbamates under the same conditions,[22,23] but in this case the yield of the product of the insertion of the nitrene in a C–H bond of dioxane proved to be fairly low and the main reaction product was the corresponding carbamate:

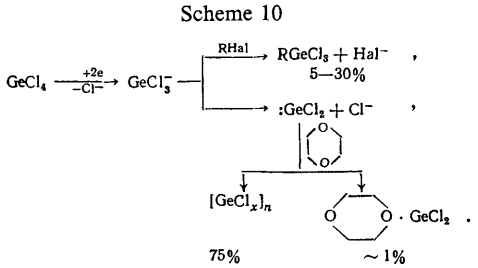
Scheme 9



Such a ratio of the electrolysis products is most probably due to the increased lability of the intermediate anion $ROCONCl^-$. In the case considered, the anion (IIa) (see Scheme 2) can fragment at the instant of its formation in the immediate vicinity of the surface of the electrode. The electron-deficient carbene-type or nitrene-type intermediate formed under these conditions is rapidly reduced at the electrode without having sufficient time to enter into the chemical reaction with the added substrate. The latter process can, in principle, partly compete with the reduction process. This (or a similar) situation evidently actually occurs in the electrolysis of *NN*-dichlorocarbamates (Scheme 9).

Germylenes. The electrochemical approach proved to be promising also for the generation of carbene analogues such as germylenes. This approach is based[25] on the electrochemical reduction of the readily available tetrachlorogermane, which had not been investigated previously. It has been established by methods involving the rotating disc electrode with a ring and electrolysis at a controlled potential [Pt cathode, AN with NEt_4ClO_4 as the supporting electrolyte, $E = -0.5$ V (rel. Ag/Ag^+)] that two electrons are transferred in the first stage of the electrochemical reduction of $GeCl_4$ with formation of the thermodynamically unstable anion $GeCl_3^-$:

Scheme 10



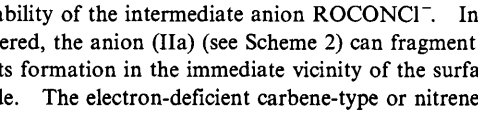
The formation of $GeCl_3^-$ has been confirmed,[26] in particular, by its interaction with organic halogeno-compounds added to the electrolysed solution. In the absence of RX (X = halogen), the $GeCl_3^-$ anion fragments with formation of a labile dichlorogermylene and then germanium subchlorides in 75% yield.[21] The intermediate formation of dichlorogermylene is demonstrated by its familiar[27] reaction with dioxane (Scheme 10), which leads to the formation of a stable complex.

3. The reduction of carbenes and nitrenes

It is quite evident that, since carbenes are electron-deficient species, they should be readily reduced. Therefore the very possibility of the cathodic generation of carbenes, which is at first sight surprising, depends on the lifetime of the intermediate carbanion (IIa) (see Scheme 2). In the case of extremely unstable anions, the carbene (or nitrene—see Section 2) formed on their fragmentation disappears rapidly via a cathodic reaction without having sufficient time to interact with a suitable substrate.

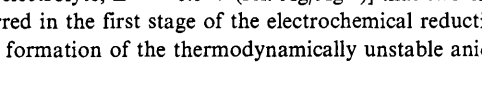
The mechanism of the cathodic reduction of carbenes was first discussed by McDonald and co-workers.[28,29] The authors chose as objects of their investigation diazo-compounds and no longer polyhalogeno-derivatives. It was postulated that the addition of an electron [$E_{p/2} = -1.68$ V (sat. c. e.), Pt cathode, DMF, NEt_4Br] initiates the fragmentation of these substances with evolution of a N_2 molecule, as happens, for example, during thermolysis. Their investigations made it possible to put forward the following mechanism of the reduction of diphenyldiazomethane:[28]

Scheme 11



A similar mechanism has been proposed for the formation and subsequent reactions of the fluorenylidene radical-anion.[29] However, a more careful investigation of this process by high-temperature cyclic voltammetry showed that diazofluorene is reduced via a stage involving the dimerisation of the radical-anion of the diazo-compound.[30]

In subsequent studies,[31,32] it was shown by chronoammetry and low-temperature controlled potential electrolysis that the reduction of $(EtO_2C)_2CN_2$ and 2-diazo-5,5-dimethylcyclohexa-1,3-diene (diazodimedone) does indeed proceed with formation of the radical-anions of diazo-compounds. These radical-anions subsequently eliminate a N_2 molecule via a first-order reaction ($k = 8 \pm 2$ s^{-1} and 1.0 ± 0.1 s^{-1} at –38° and –84 °C respectively), forming carbene radical-anions:

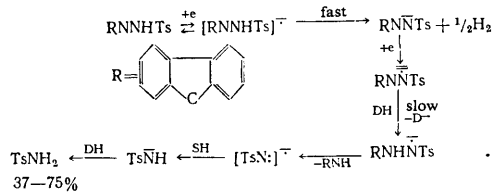


(*a*) $E_{p/2} = -1.0$ V [rel. Cd(Hg)/$CdCl_2$), cathode—vitreous carbon, DMF, NBu_4ClO_4; (*b*) $R_{p/2} = -1.82$ V (rel. Pt), Pt cathode, PrCN, NBu_4ClO_4.

In the absence of a proton donor, the above carbene radical-anions $[Y:]^-$ abstract preferentially a hydrogen atom, which leads to YH^-, while in the presence of benzoic acid, guanidinium perchlorate, or $(CF_3)_2CHOH$ they afford compounds of the type YH_2:

The carbene radical-anion $[PhC(O)\ddot{C}Ph]^-$, whose most characteristic reaction is the abstraction of a hydrogen atom from the solvent, is formed via a similar mechanism.[31] The formation

of the tosylnitrene radical-anion in the electrochemical reduction of fluorenone tosylhydrazone [$E_{p/2}$ = –0.28 V (sat. c. e.), Pt cathode, DMF, NBu_4ClO_4] was demonstrated recently with the aid of cyclic voltammetry, chronoammetry, and electrolysis at a controlled potential:[32]



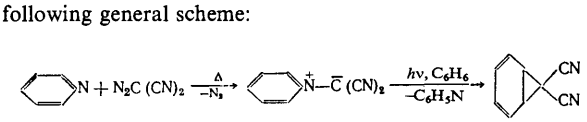
Thus the data presented above indicate the possibility of the generation and investigation of the properties of carbene and nitrene radical-anions. It may be expected that studies in this field will continue, especially to determine the oxidation-reduction as well as the electrophilic properties of carbenes and nitrenes.

III. Oxidation processes

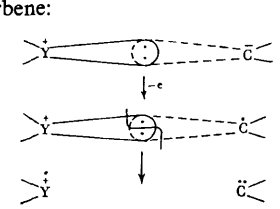
In the examples quoted above (see Section II), the electrochemical approach to the investigation of carbenes and their analogues was achieved in almost all cases via the generation of the corresponding thermodynamically unstable anions. However, from the methodological standpoint, one may be concerned with the electrochemical generation of not only anionic intermediates but also any other intermediates, whose fragmentation would be accompanied by the formation of carbenes. Data for the formation of such intermediates in the electrochemical oxidation of organic substances available at present are examined below.

1. Generation of carbenes

Ylides are known[1] to be formed or to behave as intermediates in many reactions of carbenes, carbenes with electron-accepting substituents leading to stable ylides. At the same time, even stable ylides can again become sources of carbenes on irradiation or under the influence of heat. For example, the processes described by Rieser and Friedrich[35] and by Streith et al.[36] can be represented by the following general scheme:



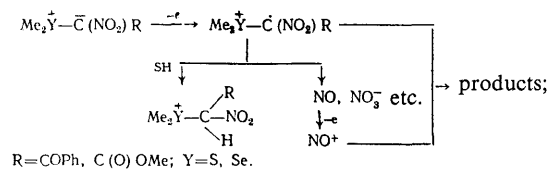
Thus the problem of generating carbenes from stable ylide structures reduces to breaking the ylide linkage in the required way by employing some kind of method involving a physical influence. One of such possibilities consists in the electrochemical oxidation of the ylide to the corresponding radical-cation, whose fragmentation would lead to a carbene:



Nitromethylides were selected as the objects of study.[37–39] The interest in these compounds was due to the possibility of generating a nitrocarbene in this way. The attempts to obtain nitrocarbenes from the corresponding α-nitrodiazo-compounds[40,41] or the alkali metal salts of polynitro- and halogenopolynitro-alkanes[42,43] proved unsuccessful.‡ Perhaps only the report[44] of the probable generation of arylnitrocarbenes from the silver salts of aryldinitromethanes is well founded: the thermolysis (at 100 °C) of these salts in the presence of alkenes leads mainly to isoxazoline *N*-oxide—the product of the 1,3-dipolar addition of an arylnitrocarbene.

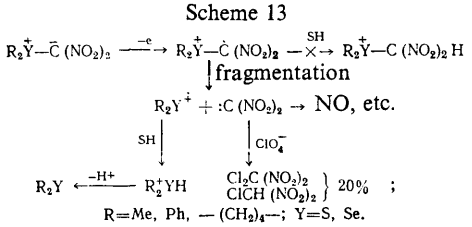
It has been shown[45] that on the polarisation curves for sulphonium§ and selenonium mononitromethylides, recorded at a platinum anode in AN in the presence of $LiClO_4$ as the supporting electrolyte, there is a single oxidation wave with $E_{1/2}$ = 1.4–1.5 V (rel. Ag/0.1 N Ag^+), its position depending on the structure of the ylide. However, the interaction of the radical-cations produced by the one-electron oxidation of the above ylides at E = 1.6 V (rel. Ag/0.1 N Ag^+) with the solvent, in which a hydrogen atom is abstracted and onium structures are formed, is faster than their fragmentation:[45]

Scheme 12



A number of indirect data[45] have indicated the possibility of the partial fragmentation of the mononitromethylide radical-cations during prolonged electrolysis, but the Y–C bond (Scheme 12) is not then involved. Thus the attempts to obtain nitrocarbenes by the anodic oxidation of nitromethylides were unsuccessful. The electrochemical oxidation of dinitromethylides (Scheme 13) yielded different results:

Scheme 13



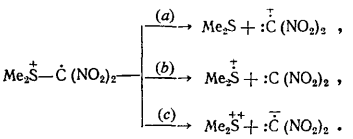
In the course of a study by the disc electrode method with a ring at an annular electrode, the formation of Me_2S was detected at the instant when dimethylsulphonium dinitromethylide was oxidised at the disc electrode; furthermore chloro-derivatives of dinitromethane were isolated from the products of the electrolysis [E = 1.9 V (rel. Ag/0.1 N Hg^+)] of the above dinitromethylide.[37] These data permit the conclusion that the intermediate radical-cation (see

‡ After the present review had been written, the formation of a nitrocarbene intermediate in the interaction of nitrodiazomethane with electron-enriched alkenes in the presence of rhodium acetate became known (P E O'Bannon, W P Dailey, *Tetrahedron Lett.*, 1988, **29** 987).

§ These conditions were standard for all the experiments described in this Section.

Scheme 13) fragments with retention of the sulphide and dinitromethyl fragments, i.e. at the Y—C bond.

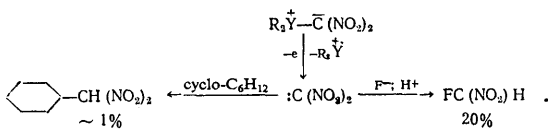
Scheme 14



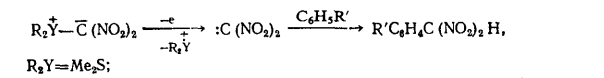
The enthalpies of the possible fragmentation pathways have been calculated in relation to the dimethylsulphonium dinitromethylide radical-cation by the MINDO/3 method.[37] The calculation showed that pathways (*a*) and (*c*) are more endothermic by 268 ± 63 and 1239 ± 63 kJ mol^{-1} than pathway (*b*) leading to the formation of a dinitrocarbene (Scheme 14). According to the calculated data, the dinitrocarbene has a singlet ground state, which is more favourable than the triplet state (the difference is 26 kJ mol^{-1} [37]).

A convenient criterion for the quantitative description of the electrophilicity of carbenes is known[46,47] to be the energy of the LUMO. This permits the calculation, within the framework of the MINDO/3 method, of the electronic structures of a series of singlet carbenes of the type :CR_2 [R = OH, F, Cl, CN, C(O)H, or NO_2] and makes it possible to demonstrate[37] that dinitrocarbene is the most electrophilic carbene in the series considered, because it has the lowest energy of the LUMO. This conclusion was then justified experimentally by introducing the electrochemically generated dinitrocarbene into reactions characteristic of electrophilic carbenes.[38,39]

The carbene mechanism explains satisfactorily the nature of the products formed in the electrochemical oxidation of dinitromethylides in the presence of cyclohexane and the fluoride ion:[38]

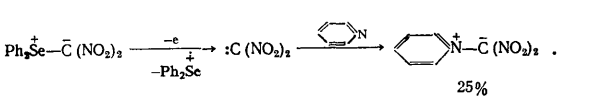


Like other electrophilic carbenes, dinitrocarbene interacts with the aromatic ring. The formation of the corresponding aryldinitromethanes can be explained by the insertion of dinitrocarbene in a C—H bond of the aromatic ring:[38]

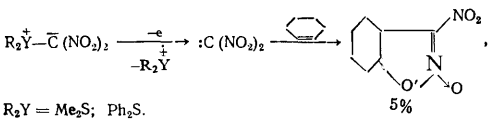


$R_2Y = Me_2S$;
R′ = H (yield 50%), Cl (40%), CN (15%), NO_2 (10%).

This process occurs even in the presence of substrates deactivated with respect to electrophilic attack. The electrolysis of dinitromethylides in the presence of pyridine entails the transylidation process:[39]



Another process characteristic of carbenes is their addition to a C=C bond. Calculation by the MINDO/3 method[38] for the interaction of dinitrocarbene with ethylene showed that the 1,3-addition of dinitrocarbene is preferable to the cyclopropane formation reaction. This conclusion agrees with data for the anodic electrolysis of dinitromethylides in the presence of cyclohexene:[38]

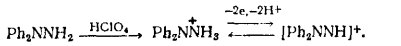


$R_2Y = Me_2S$; Ph_2S.

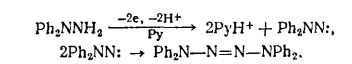
For comparison we may note that the dinitromethyl radical, which is also a highly electrophilic species,[48] generated by the electrochemical oxidation of the dinitromethane anion, either does not enter at all into reactions similar to those discussed above or it forms products in much lower yields.

2. Generation of carbene analogues

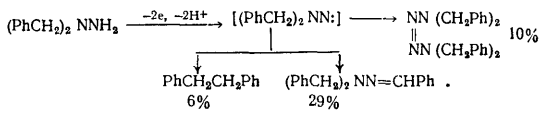
Nitrenes. Under anodic oxidation conditions, it is possible to generate also species such as nitrenes. As early as the beginning of the 1970's, investigators[49,50] studying the electrochemical oxidation of 1,1-disubstituted hydrazines concluded that this process includes a stage involving the intermediate formation of nitrenes. In this case, the anodic activation of the substrate is accompanied by fragmentation of a different type from that described in subsection 1, namely the elimination of protons. This conclusion is confirmed by data for the oxidation of 1,1-diphenylhydrazine at a platinum anode. In acidified (by the addition of $HClO_4$) AN, this process leads to the quantitative formation of the diphenyldiazenium cation (a protonated nitrene), which can be fully reconverted into the initial hydrazine by electrochemical reduction:[49]



On the other hand, in the presence of pyridine (Py), which facilitates the deprotonation of the intermediate radical-cations, the oxidation of 1,1-diphenylhydrazine proceeds via the formation of a nitrene, which rapidly dimerises to afford a quantitative yield of tetraphenyltetrazene:



Subsequently it was shown[51–53] that the electrochemical oxidation of *NN*-dibenzylhydrazine at E = 0.16 V (rel. Ag/Ag^+) at a platinum anode in AN in the presence of NBu_4BF_4 as the supporting electrolyte leads to bibenzyl, 1,1,4,4-tetrabenzyl-2-tetrazene, and benzaldehyde dibenzylhydrazone in material yields of 6, 10, and 29% respectively.[51] The mechanism of the formation of these substances includes stages with participation of a nitrene as a reactive intermediate:

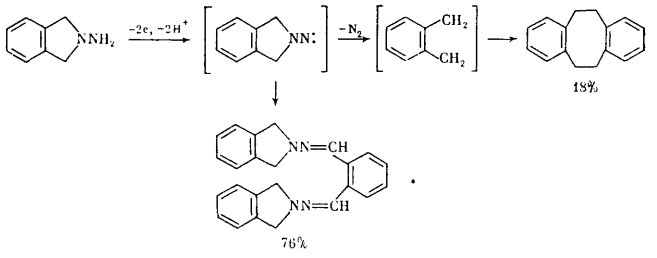


When the process is carried out on graphite (E = 0.37 V), tetrazene and the hydrazone are formed in 11 and 49% yields respectively, while bibenzyl is formed only in trace amounts.[51].

The electrochemical oxidation of *N*-aminodihydroisoindole at a platinum anode in the aprotic medium (AN) in the presence of the NBu_4BF_4 supporting electrolyte leads to 1,2,5,6-dibenzo-1,5-cyclooctadiene and a substituted *o*-xylylene[51,52] in current yields of 18 and 76% respectively. It is suggested that the two-electron oxidation of *N*-aminodihydroisoindole proceeds via the formation of a metastable

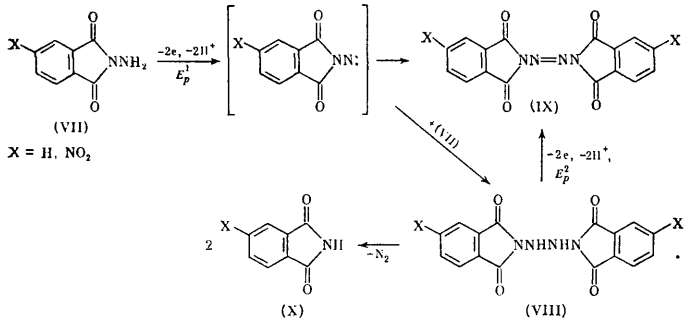
nitrene-type intermediate. The latter either splits off a N_2 molecule, forming a biradical whose dimerisation leads to a cyclooctadiene derivative, or gives rise to an *o*-xylene derivative via a complex mechanism:

Scheme 15



The electrochemical oxidation of *N*-aminophthalimide and of its tetrachloro- and 3-nitro-derivatives has been investigated[53] by cyclic voltammetry and electrolysis at a controlled potential (Pt anode, 0.1 N NBu_4BF_4 or 0.4 N $LiClO_4$ supporting electrolyte in AN). It was established that these compounds are oxidised in the first stage [E_p^1 = 0.99, 1.31, and 1.20 V (rel. Ag/Ag^+) respectively] with transfer of two electrons and two protons to the corresponding nitrenes, whose subsequent reactions lead to 1,4-diphthalotetrazans and 1,4-diphthalotetrazenes. In the second stage ($E_p^2 \geqslant 1.68$ V), the tetrazan is oxidised to the tetrazene. The overall process is described by Scheme 16:

Scheme 16



The yields and ratios of the products depend on the electrolysis conditions (Table 3). The tetrazene (IX) can be obtained also under conditions excluding the possibility of the electrochemical oxidation of the tetrazan (VIII) to the tetrazene (IX) (the controlled electrolysis potential is in the range of the E_p^1 potentials), which confirms the intermediate formation of a nitrene. During electrolysis, the tetrazan (VIII) decomposes partly with elimination of N_2, affording the product (X).

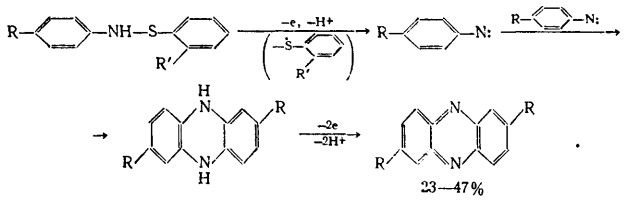
Table 3 shows that electrolysis at higher anodic potentials leads mainly to the formation of the tetrazene (IX), because the tetrazan (VIII), formed as a result of the insertion of the nitrene in a N—H bond of the initial aminophthalimide, is oxidised at the electrode to the tetrazene (IX). It is of interest to note that electrolysis at the potentials of the first wave in the presence of the NBu_4BF_4 supporting electrolyte leads preferentially to the formation of the tetrazan (VIII), while in the presence of the $LiClO_4$ supporting electrolyte the tetrazene (IX) is formed preferentially. Evidently ionic association effects influence significantly the mode of the reactions with participation of the intermediate nitrene. This question merits special consideration. At any rate, the examples presented demonstrate clearly the possibility of controlling the oxidation process (Scheme 16) depending on the electrolysis conditions.

Table 3. Yields of the products of the anodic oxidation of *N*-aminophthalimide (RH) and its nitro-derivative (RNO_2).[53]

Starting material	Supporting electrolyte	*E* in electrolysis, V(rel. Ag/Ag^+)	*Q*, F mol^{-1}	Current (material) yield		
				(VIII)	(IX)	(X)
RH	0.1 *N* NBu_4BF_4	1.3	0.5	80 (40)	—	—
RH	0.1 *N* NBu_4BF_4	1.9	0.5	0	64 (16)	—
RH	0.4 *N* $LiClO_4$	1.3	0.8	9 (6)	66 (27)	15 (12)
RH	0.4 *N* $LiClO_4$	2.0	1.0	0	86 (43)	10 (10)
RNO_2	0.4 *N* $LiClO_4$	1.3	0.8	0	51 (21)	29 (24)
RNO_2	0.4 *N* $LiClO_4$	2.0	1.0	0	64 (32)	21 (21)

Note. The oxidation was carried out at a platinum anode in AN.

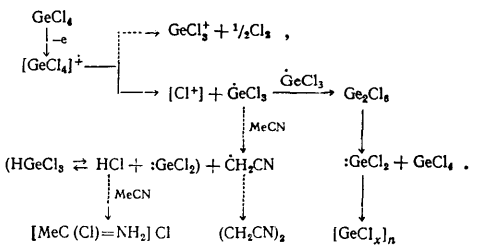
The nitrene can be generated under the conditions of anodic electrolysis also by the electrochemical oxidation of 2,4′-substituted benzenesulphenanilides.[52] On a graphite cathode in AN in the presence of the $NaClO_4$ supporting electrolyte, this process takes place with abstraction of one electron and leads to the cleavage of the S—N bond in the intermediate radical-cation (see Section II. 1). The nitrene formed enters into a intermolecular reaction involving insertion in a C—H bond, producing an adduct, which is subsequently oxidised at the electrode with transfer of two electrons and two protons, affording a phenazine:[52]



It is noteworthy that the electrochemical oxidation of *N*-aminophthalimides (see above) can compete successfully with the chemical methods for the synthesis of relatively unstable 2,3-unsubstituted tetrazans and tetrazenes, while the electrochemical oxidation of 4-substituted benzenesulphenanilides constitutes in essence a new method of synthesis of 2,7-disubstituted phenazines, which are otherwise difficult to obtain.[54–59]

Germylenes. According to Petrosyan et al,[26] dichlorogermylene is formed not only in the cathodic reduction of $GeCl_4$, as a result of the fragmentation of the intermediate anion $GeCl_4^-$ (see Section II, subsection 2), but also in the anodic oxidation of $GeCl_4$. The mechanism of the electrochemical oxidation of $GeCl_4$ (Pt anode, AN, $LiClO_4$) can be described[26] by the following scheme (the dashed

lines indicate minor processes) on the basis of data obtained by methods involving a rotating disc electrode with a ring and electrolysis at a controlled potential:



The intermediate radicals $\dot{G}eCl_3$ dimerise rapidly, affording Ge_2Cl_6, which readily disproportionates with formation of dichlorogermylene. The latter has been detected as a stable complex with dioxane (see Section II, subsection 2). The preparative electrolysis is accompanied by the formation of germanium subchlorides from dichlorogermylene in 60% yield. The intermediate radicals $\dot{G}eCl_3$ are capable of abstracting a hydrogen atom from AN, giving rise to $\dot{C}H_2CN$ and $HGeCl_3$, which indicates the presence in the reaction mixture of trace amounts of $(CH_2CN)_2$ and $[CH_3C(Cl)=NH_2]Cl$.

In conclusion, we may note that the observed ability of $GeCl_4$ to function as a source of dichlorogermylene under the conditions of both cathodic and anodic processes merits special attention and the development of electrochemical studies on these lines should lead to new interesting findings. The latter may prove valid also for the tetrachlorides of other Group IV elements, which have been hardly studied hitherto.

References

1. M Makosha, M Fedorynski *Zh. Vses. Khim. Ova im D I Mendeleeva*, 1979, **24**(5) 466
2. A V Bukhtiyarov, E A Chernyshev, O V Kuz'min, et al. *Dokl. Akad. Nauk SSSR*, 1984, **278**(5) 1127
3. S Wawsonek, R C Duty *J. Electrochem. Soc.*, 1961, **108** 1135
4. H P Fritz, W Kornrumpf *Liebigs Ann. Chem.*, 1978, 1416
5. H P Fritz, W Kornrumpf *J. Electroanal. Chem. Interfacial Electrochem.*, 1979, **100** 217
6. H P Fritz, W Kornrumpf *J. Electrochem. Soc.*, 1980, **127** 128
7. G P Girina, V A Kokorekina, L G Feoktistov, et al. *IX Vsesoyuznoe Soveshchanie po Polyarografii: Tezisy Dokladov* (IX All-Union Conference on Polarography), Ust'-Kamenogorsk, 1987, Part 1, p. 137
8. M M Baizer, J L Chruma *J. Org. Chem.*, 1972, **37** (12) 1951
9. A J Fry, R G Reed *J. Am. Chem. Soc.*, 1972, **94**(24) 8475
10. E H Mottus, M R Ort *J. Electrochem. Soc.*, 1970, **117** 885
11. V A Afanas'ev, O S Korneva, G N Nesterenko, et al. *IV Vsesoyuznaya Konferentsiya po Khimii Karbenov: Tezisy Dokladov* (The IV All-Union Conference on the Chemistry of Carbenes: Abstracts of Reports), Izd. Nauka, Moscow, 1987, p. 112
12. R C Duty, G Biolchini, W Matthews *Anal. Chem.*, 1974, **46** 167
13. R C Duty, B V Pepich *J. Electrochem. Soc.*, 1980, **127** 1261
14. V A Petrosyan, M E Niyazymbetov, T K Baryshnikova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 91
15. T K Baryshnikova, M E Niyazymbetov, V S Bogdanov, V A Petrosyan *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 2325
16. J Tabushi, Z Yoshida, N Takahashi *J. Am. Chem. Soc.*, 1971, **93** 1820
17. M Makosza, A Kacprowicz *Rocz. Chem.*, 1975, **49** 1627
18. W E Parham, J R Potoski *Tetrahedron Lett.*, 1966, 2311
19. M Saunders, R W Murray *Tetrahedron*, 1960, **11** 1
20. V A Petrosyan, M E Niyazymbetov, T Yu Rudashevskaya, L V Adaevskaya *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 2183
21. T Fuchigami, T Nonaka, K Iwata *J. Chem. Soc., Chem. Commun.*, 1976, 951
22. T Fuchigami, T Nonaka *Chem. Lett.*, 1977, 1087
23. T Fuchigami, T Nonaka *Inform. Mater. Energy Theory Life*, 1985, **53** 582
24. D S Breslow *Nitrenes* (Edited by W Lwowski), Intersci. Publ., 1970, p. 287
25. V A Petrosyan, M E Niyazymbetov, S P Kolesnikov, V Ya Li *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 461
26. V A Petrosyan, M E Niyazymbetov, S P Kolesnikov, V Ya Li *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 1889
27. O M Nefedov, S P Kolesnikov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1966, 201
28. R N McDonald, J R January, K J Borhani, M D Hawley *J. Am. Chem. Soc.*, 1977, **99** 1268
29. R N McDonald, K J Borhani, M D Hawley *J. Am. Chem. Soc.*, 1978, **100** 995
30. V D Parker, D Bethell *Acta Chem. Scand. Ser. B*, 1980, **34** 617
31. D A van Galen, M P Young, M D Hawley, R N McDonald *J. Am. Chem. Soc.*, 1985, **107** 1465
32. D A van Galen *J. Electrochem. Soc.*, 1986, **133** 441
33. D Bethell, L J McDowall, V D Parker *J. Chem. Soc., Chem. Commun.*, 1984, 308
34. D A van Galen, J H Barnes, M D Hawley *J. Org. Chem.*, 1986, **51** 2544
35. J Rieser, K Friedrich *Liebigs Ann. Chem.*, 1976, **764** 666
36. J Streith, A Blind, J M Cassal, C Sigwalt *Bull. Soc. Chim. Fr.*, 1969, 948
37. V A Petrosyan, M E Niyazymbetov, V D Semenov, et al. *IV Vsesoyuznaya Konferentsiya po Khimii Karbenov: Tezisy Dokladov* (The IV All-Union Conference on the Chemistry of Carbenes: Abstracts of Reports), Izd. Nauka, Moscow, 1987, p. 112
38. V A Petrosyan, M E Niyazymbetov, V V Semenov, et al. *IV Vsesoyuznaya Konferentsiya po Khimii Karbenov: Tezisy Dokladov* (The IV All-Union Conference on the Chemistry of Carbenes: Abstracts of Reports), Izd. Nauka, Moscow, 1987, p. 116
39. V A Petrosyan, V N Solkan, M E Niyazymbetov, et al. *IV Vsesoyuznaya Konferentsiya po Khimii Karbenov: Tezisy Dokladov* (The IV All-Union Conference on the Chemistry of Carbenes: Abstracts of Reports), Izd. Nauka, Moscow, 1987, p. 114
40. U Schöllkopf, P Markush *Liebigs Ann. Chem.*, 1971, **753** 143
41. U Schöllkopf, P Markush *Liebigs Ann. Chem.*, 1971, **753** 147
42. K Torssell, R Rynode *Ark. Kemi.* , 1965, **25**(6) 625
43. A Rahman, L Clapp *J. Org. Chem.*, 1976, **41** 122
44. E Contouli-Argyropoulon, N E Alexandron *J. Org. Chem.*, 1980, **45** 4158
45. M E Niyazymbetov, V A Petrosyan, V V Semenov, S A Shevelev *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 1332
46. R Moss *Acc. Chem. Res.*, 1980, **13** 58
47. S Stinson *Chem. Eng. News*, 1979, **57** 20

48. V A Petrosyan, M E Niyazymbetov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 368
49. G Gauguis, M Genies *Tetrahedron Lett.*, 1970, 2903
50. G Gauguis, B Chaband, M Genies *J. Electroanal. Chem. Interfacial Electrochem.*, 1972, **40** 6
51. T Fuchigami, T Sato, T Nonaka, J K Lee *J. Chem. Soc. Jpn., Chem. Ind. Chem.*, 1984, (11) 1769
52. T Fuchigami, T Nonaka *Denki Kagaku*, 1983, **51**(1) 133
53. T Fuchigami, T Sato, T Nonaka *Electrochem. Acta*, 1986, **31** 365
54. H Sayo, K Mori, A Ueda, N Morimoto *Chem. Pharm. Bull.*, 1977, **25** 525
55. H Sayo, K Mori, A Ueda, T Michida *Chem. Pharm. Bull.*, 1978, **26** 1682
56. H Sayo, K Mori, T Michida *Chem. Pharm. Bull.*, 1979, **27** 2316
57. H Sayo, K Mori, T Michida *Chem. Pharm. Bull.*, 1980, **28** 3707
58. H Sayo, K Mori, T Michida *Chem. Pharm. Bull.*, 1981, **29** 2598
59. H Sayo, K Mori, T Michida *Chem. Pharm. Bull.*, 1982, **30** 3782