U.D.C. 543.878:547.565

Reactions of Sterically Hindered Phenols and Their Derivatives with Transfer of one Electron

V.V.Ershov, A.A.Volod'kin, A.I.Prohof'ev, and S.P.Solodovnikov

The reactions of sterically hindered phenols (phenoxides) and their derivatives (phenoxy-radicals and cyclohexadienones), in the first step of which the transfer of one electron is possible, have been examined. To confirm the hypothesis concerning the mechanism of organic reactions with transfer of one electron†, kinetic data and the results of the polarographic analysis and investigation of the reactions under discussion by physicochemical methods are presented. Certain reactions of sterically hindered phenols and their derivatives the investigators of which supported previously a different mechanism have been analysed critically from the standpoint of the mechanism involving the transfer of one electron.
The bibliography includes 124 references.

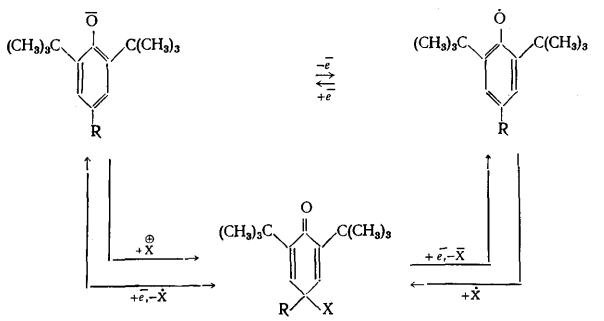
CONTENTS

1. Introduction 740
2. Sterically hindered phenols (phenoxides) 741
3. Sterically hindered phenoxy-radicals 743
4. Sterically hindered cyclohexadienones 744

1. INTRODUCTION

A characteristic feature of sterically hindered phenols and their derivatives (phenoxy-radicals and cyclohexadienones) is a wide variety of phenol—diene and dienone—phenol interconversions. Thus, when sterically hindered phenols interact with electrophilic agents (bromination, nitration, and nitrosation), cyclohexadienones (quinolide compounds) are frequently formed. Similar cyclohexadienones are also the main products in radical reactions of sterically hindered phenols. Cyclohexadienones are as a rule extremely reactive and are capable of being converted into compounds with a phenolic structure as a result of their reactions with the majority of reagents.

The results of studies in recent years on sterically hindered phenols, phenoxy-radicals, and cyclohexadienones have led to the conclusion that phenol—dienone and dienone—phenol interconversions frequently proceed via a stage involving the transfer of one electron. The possibility of this mechanism is primarily due to the distinct electron-donating properties of phenols (particularly phenoxides) as well as the typical electron-accepting properties of phenoxy-radicals and cyclohexadienones:



Comparison of the results of the polarographic analysis of phenols, phenoxy-radicals, and cyclohexadienones with their structure and with the kinetic data for reactions in which these species are involved has shown that in many cases one-electron transfer may be regarded as an alternative to the homolytic reaction mechanism. Finally, the relative stability of phenoxy-radicals, phenoxides and the majority of quinolide compounds permits their employment as convenient models for the investigation of various aspects of reactions proceeding with transfer of one electron.

This review deals with data obtained both in the study of model reactions having a clearly demonstrated one-electron transfer stage as well as certain reactions which are of great theoretical importance and in which the one-electron transfer stage has not so far been detected by the existing methods but whose results can be satisfactorily accounted for by postulating the involvement of one electron in the first step of the chemical process. Naturally the discussion of such reactions and conclusions concerning them can be only qualitative. This approach to the study of reactions of sterically hindered phenols and their derivatives is nevertheless apparently justified, since it frequently makes it possible to explain the formation of products which previously did not fit within the framework of the hypotheses adopted. Moreover, such reactions, for example, those of phenoxy-radicals with amines, phosphites, and other substances are in general difficult to understand without considering the electron-donating and electron-accepting properties of the reactants. Thus the rate constant for the reaction of the tri-t-butylphenoxy-radical with ethylbenzene, accompanied by the homolytic elimination of a hydrogen atom from the substrate, is 10^{-7} litre mole^{-1} s^{-1} (E_{act} = 17 kcal mole^{-1}) at room temperature, while for the reaction of the same radical with triethylamine, the energy of the C—H bond in which should not differ markedly from that in ethylbenzene, the rate constant at same temperature is 10^{-4} litre mole^{-1} s^{-1} (E_{act} = 13.3 kcal mole^{-1}). It is noteworthy that in both cases the main final reaction product is tri-t-butylphenol[1,2].

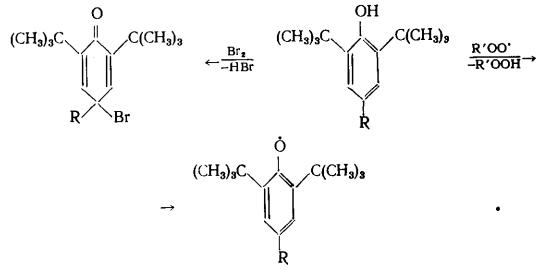
Thus examination of numerous reactions in which phenols, phenoxides, phenoxy-radicals, and quinolide compounds are involved from the standpoint of one-electron transfer may prove to be fruitful both in creating new model systems for the investigation of the mechanisms of

† See K. A. Bilevich and O. Yu. Okhlobystin, Uspekhi Khim., 37, 2162 (1968) [Russ. Chem. Rev., No. 12 (1968)].

organic reactions and of the search for ways of synthesising compounds which have not as yet been described. In connection with the high specificity of the behaviour of these compounds in reactions with one-electron transfer, it is most convenient to examine separately the properties of phenols (phenoxides), phenoxy-radicals, and cyclohexadienones in these processes.

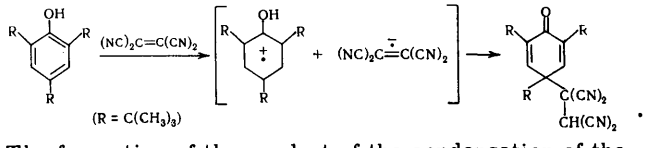
2. STERICALLY HINDERED PHENOLS (PHENOXIDES)

The hypothesis of the decisive role of the stability of the phenolic O—H bonds in reactions of sterically hindered phenols is nowadays generally accepted. It is assumed that, depending on the nature of the other reactant, the bond can be broken either homolytically[3-5] (for example in inhibited oxidation processes) or heterolytically, as in the interaction of sterically hindered phenols with electrophilic agents[6-8] (bromination, nitration and other reactions):

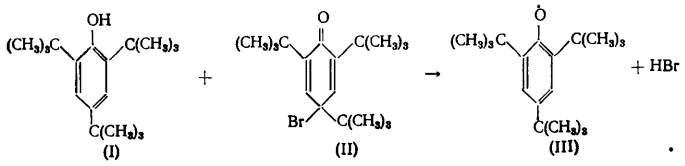


However, despite the important role of the O—H bond energy in the treatment of the mechanism of reactions of sterically hindered phenols, its value has been determined only for certain of the simplest alkylphenols[9,10].

The involvement of the hydrogen atom of the phenolic hydroxyl in the initial step in chemical reactions of sterically hindered phenols was unquestioned until recently, although there existed an alternative mechanism of this process, namely one involving reactions with transfer of one-electron. The formation of a complex, within which there is a formal possibility of the transfer of one electron has been begun to be postulated recently even for classical radical reactions such as the interaction of peroxy-radicals with sterically hindered phenols[11]. The transfer of one electron as one of the elementary steps of the chemical interaction can be postulated for reactions of sterically hindered phenols with reactants exhibiting a high electron affinity. Thus, when alkylphenols react with quinones[12] and quinolide compounds[13-15], phenoxy-radicals are formed. An analytical method for the determination of phenols is based on the reaction of sterically hindered phenols with tetracyanoethylene[16]:

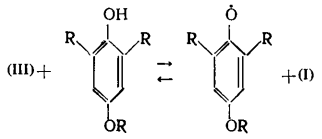


The formation of the product of the condensation of the phenol with tetracyanoethylene agrees fairly well with the possibility of the transfer of one electron in the first reaction stage. It has been shown for the reaction of 2,4,6-tri-t-butylphenol (I) with 4-bromo-2,4,6-tri-t-butylcyclohexa-2,5-dienone (II), which leads to only one product—the stable phenoxy-radical (III), that its rate is independent of the nature of the solvent and that there is no isotope effect when compound (II) is allowed to react with the phenol(I) deuterated in the phenolic hydroxyl[13]:



It follows from the kinetic data obtained for the interaction of 2,4,6-tri-t-butyl-4-nitrocyclohexa-2,5-dienone with various phenols that its activation energy depends significantly on the nature of the *para*-substituent in the phenol molecule and that it increases as the electron-accepting properties of the *para*-substituent are enhanced[15].

A typical homolytic reaction of sterically hindered phenols with phenoxy-radicals may be treated formally as a reaction in which there is an electron transfer from the phenol to the radical. If two stable radicals with approximately identical oxidation-reduction potentials are involved in this reaction, the latter is reversible[17]:



(R = C(CH$_3$)$_3$)

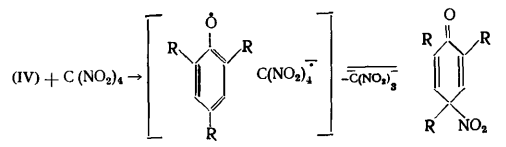
Studies on the transfer of a hydrogen atom between a phenol molecule and the corresponding phenoxy-radical by ^{1}H NMR have shown the possibility of the existence of an intermediate complex[18,19]. According to the views of Müller et al., this complex is an ion pair (see Section III) in which there is a transfer of one electron[20].

In contrast to sterically hindered phenols, their phenoxides have more marked electron-donating properties. For example, while the half-wave potential for the anodic oxidation of compound (I) is 1.0 V, the half-wave potential for the anodic oxidation of 2,4,6-tri-t-butylphenoxide (IV) is already in the region of zero potential[21-23]. The salts of sterically hindered phenols have been frequently used as nucleophilic components in order to confirm the hypothesis of the possibility of one-electron transfer in the interaction of two non-radical species[24-27]. Moreover, in the light of the mechanism involving one-electron transfer, the results of reactions investigated earlier, such as the oxidation of sterically hindered phenols by molecular oxygen in an alkaline medium[28-30] and the interaction of phenoxides with various reactants involving the formation of compounds characteristic of radical reactions[31,32] (the dimerisation and disproportionation products from phenoxy-radicals) become understandable.

The one-electron transfer stage in the reaction between the anion and a neutral molecule has been demonstrated by the formation of a radical and the corresponding radical-anion. In the reactions of (IV) with tetracyanoethylene[33], chloranil[33], and difluorodinitromethane[24], radicals were detected by ESR:

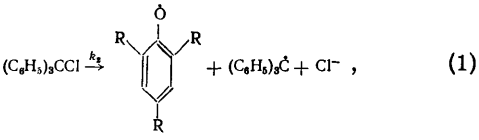
$$(IV) + CF_2(NO_2)_2 \rightarrow (III) + CF_2(NO_2)_2^{\cdot-}.$$

The nitration of (IV) by tetranitromethane probably proceeds by a similar mechanism[26]:

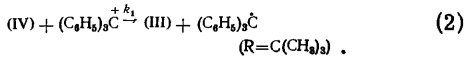


(R=C(CH$_3$)$_3$)

The study of the kinetics of the reaction of potassium 2,4,6-tri-t-butylphenoxide with chlorotriphenylmethane (trityl chloride) showed[25] that the formation of compound (III) in this case is possible via electron transfer from the phenoxide ion both to trityl chloride [reaction (1)] and to the trityl cation [reaction (2)]:



(1)



(R=C(CH$_3$)$_3$) .

According to this mechanism the initial rate of accumulation of the phenoxy-radical (III) is described by the equation‡

$$W_0 = k_1'(\mathrm{TCl}) + k_2(\mathrm{TCl})\cdot(\mathrm{ArOK})^2 \ .$$

The relative contribution of a particular mechanism depends significantly on the nature of the solvent. For example, an increase of the solvating capacity of the solvent leads to an increase of the contribution of reaction (2), while the reaction between the phenoxide (IV) and trityl chloride in heptane proceeds only as a trimolecular process [reaction (1)].[34] On passing from trityl chloride to trityl bromide, the rate of reaction with the phenoxide (IV) increases appreciably both via the monomolecular [reaction (2)] and the ter-molecular [reaction (1)] mechanisms. In the trityl chloride–phenoxide (IV) system, the transfer of one electron is much slower than in the reaction of trityl bromide with the phenoxide (IV), reaction (1) involving trityl bromide being 100 times faster and reaction (2) 50 times faster than the reaction of the radical (IV) with trityl chloride[35]. Tri-(*p*-nitrophenyl)methyl bromide reacts almost instantaneously with salts of sterically hindered phenols[35].

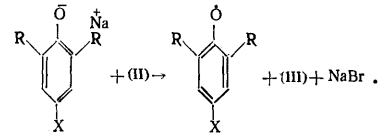
The reaction of salts of sterically hindered phenols with quinolide compounds may be regarded as a model of substitution reactions of the S_N2 type proceeding via a one-electron transfer stage[36], the activation energy of which increases in the sequence Br < Cl < NO_2 as a function of the geminal substituent in the quinolide compound. The rate of reaction depends significantly on the solvent owing to the different degrees of solvation of the metal cation by solvent molecules[36]:

$$(\mathrm{IV}) + (\mathrm{II}) \rightarrow 2(\mathrm{III}) + \mathrm{EX}$$
$$(\mathrm{X}=\mathrm{Br}, \mathrm{Cl}, \mathrm{NO_2})$$

Studies of the kinetics of the reactions of cyclohexadienone (II) (X = Br) with the sodium salts of 2,6-di-t-butylphenols containing various substituents in the *para*-position showed that, as the electron-accepting properties of the substituent become more marked, the activation energy increases and the reaction rate constant falls. This behaviour is probably related to the decrease of the effective negative charge on the oxygen atom in the phenoxide ion. The reaction does not occur with sodium 2,6-di-t-butyl-4-nitrophenoxide. The activation energy for this reaction is satisfactorily correlated with the σ_p constants of the substituents (r = 0.983; ρ = 10.2). On the other hand, this type of relation holds much less satisfactorily for the reaction rate constants[37]. The absence of a dependence of the reaction rate constants on the substituent constants may be a consequence of a compensation effect, since the pre-exponential factor for this reaction increases with activation energy (Table 1).

Table 1. Kinetic parameters of the reaction of (II) with substituted sodium 2,6-di-t-butylphenoxide in THF.

X	k (30°), litre mole^{-1} s^{-1}	k_0, litre mole^{-1} s^{-1}	E_{act} ± 0.5, kcal mole^{-1}	X	k (30°), litre mole^{-1} s^{-1}	k_0, litre mole^{-1} s^{-1}	E_{act} ± 0.5, kcal mole^{-1}
C(CH$_3$)$_3$	5·10^{-1}	4,7·10^7	11.0	COOC$_2$H$_5$	2,5·10^{-6}	3,6·10^6	16.9
C$_6$H$_5$	2·10^{-3}	2,5·10^5	11.6	COCH$_3$	1,8·10^{-5}	2,8·10^3	18.3
CHO	2,4·10^{-6}	8,0·10^4	14.5	CN	3,3·10^{-6}	2,5·10^8	19.2

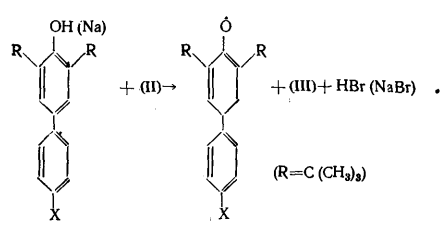


(R=C(CH$_3$)$_3$)

Comparative data for the kinetics of the reaction of (II) with 2,6-di-t-butyl-4(*p*-X-phenyl)phenols and their sodium salts have shown that the rate constants for reactions of phenols with (II) are smaller by 3–4 powers of ten than the rate constants for the analogous reactions of the corresponding phenoxide ions and the activation energies for the reactions with the phenols are almost twice as great as the energies for the reactions with their phenoxides[38] (Table 2).

Table 2. Kinetic parameters of the reaction of (II) with 2,6-di-t-butyl-4-(*p*-X-phenyl)phenols and their sodium salts in THF.

X	Phenols			Sodium phenoxides		
	10^8k, litre mole^{-1} s^{-1}	$10^{-8}k_0$, litre mole^{-1} s^{-1}	E_{act} ± 1, kcal mole^{-1}	10^4k, litre mole^{-1} s^{-1}	$10^{-5}k_0$, litre mole^{-1} s^{-1}	E_{act} ± 0.5, kcal mole^{-1}
H	2.5	0,016	19.3	1.3	3.5	11.6
C$_2$H$_5$	1.8	0.9	21.7	4.0	7.0	11.5
OCH$_3$	—	—	—	1.6	0.4	10.4
Cl	—	—	—	1.8	6.0	11.8
COCH$_3$	3.0	1.0	21.4	0.21	0.7	11.9
COOCH$_3$	2.0	2.0	22.1	0.3	11.0	10.7



(R=C(CH$_3$)$_3$)

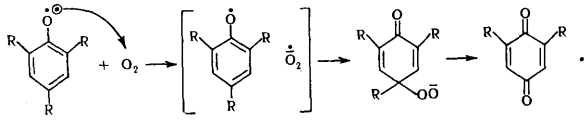
The pre-exponential factor for the reaction of (II) with sodium 2,6-di-t-butyl-4-(*p*-X-phenyl)phenoxides varies

‡ It is assumed in this equation that $k_1 > k_1'$, where k_1' is the monomolecular dissociation constant of trityl chloride.

insignificantly and for this reaction series there is satisfactory correlation between the rate constants and the σ_p constants of the substituents in the phenyl group (r = 0.994; ρ = 1.45).

Data for the reaction of sterically hindered phenols with molecular oxygen in an alkaline medium are interesting from the standpoint of one-electron transfer. The extensive factual experimental data on this question have been reviewed[39], but the mechanism of this reaction has not been discussed in detail. That it is of a radical type appears evident. During the reaction, semiquinone radicals are detected and various quinolide compounds, hydroperoxides, quinones, hydroxyquinones, and products of their further reactions are formed[39-41]. It has also been suggested[42] that the first stage in the interaction of oxygen with phenols in an alkaline medium is the formation of the phenoxy-radical.

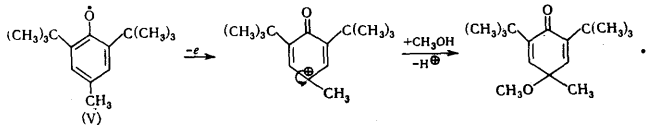
Analysis of the experimental data for the interaction of sterically hindered phenols with oxygen in an alkaline medium suggests that it does not involve a neutral molecule but the corresponding phenoxide and proceeds via a one-electron transfer mechanism. Since the phenoxy-radical and the oxygen radical-anion are formed in the "cage", the probability of their recombination increases greatly. Therefore, in the oxidation of sterically hindered phenols by atmospheric oxygen in an alkaline medium, the corresponding hydroperoxides and their decomposition products (quinones) are obtained preferentially[43,44]:



The formation of phenoxy-radicals or typical reactions products from phenoxy-radicals during the interaction of the lithium salt of 2,4,6-tri-t-butylphenol with benzenesulphenyl chloride[31] and in the interaction of potassium 2,6-di-t-butyl-4-nitrophenoxide with toluenesulphonyl chloride or chloroformate esters[32] can probably also be accounted for by one-electron transfers. It has been suggested in the literature that the reaction of salts of sterically hindered phenols with benzenediazonium chloride proceeds via a one-electron transfer stage[45].

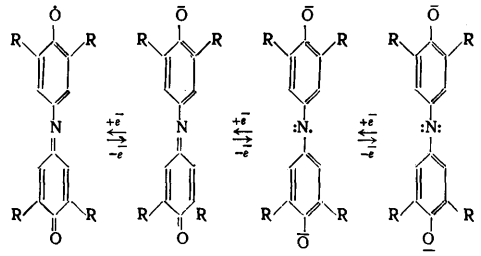
3. STERICALLY HINDERED PHENOXY-RADICALS

In contrast to phenols, which are as a rule incapable of accepting electrons the corresponding phenoxy-radicals have distinct electron-accepting properties. Extremely unstable cations, which react in the carbonium form with the solvent, are formed as intermediates only in the anodic oxidation of certain phenoxy-radicals[21-23]. For example, the anodic oxidation of the 2,6-di-t-butyl-4-methylphenoxy-radical (V) in methanol results in the formation of 2,6-di-t-butyl-4-methoxy-4-methylcyclohexa-2,5-dienone:



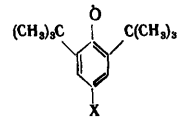
(V)

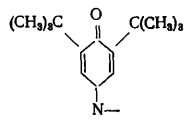
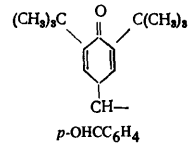
Studies on the polarographic reduction of many stable phenoxy-radicals have shown that the half-wave potentials $E'_{1/2}$ for the reduction of these radicals to the corresponding phenoxides depends on their structure and on the nature of the substituents in the phenoxy-radical (Table 3). Thus Coppinger's radical and the 2,2',6,6'-tetra-t-butylindophenoxy-radical (VI) are reduced at potentials close to zero, probably owing to the more extensive conjugation system in these radicals[46]. As a result of its structural features, the electrochemical reduction of radical (VI) entails the initial formation of a phenoxide, which is capable of accepting a further two electrons with formation of a radical-dianion and a trianion:



(VI) (R=C(CH$_3$)$_3$)

Table 3. Half-wave potentials in the polarographic reduction of the stable phenoxy-radicals[47].



X	$E'_{1/2}$, V	X	$E'_{1/2}$, V
	0.07	p-CH$_3$COC$_6$H$_4$	−0.29
		p-CH$_3$OCOC$_6$H$_4$	−0.31
		p-ClC$_6$H$_4$	−0.36
		C$_6$H$_5$	−0.37
		(CH$_3$)$_3$C	−0.38
	0.09	p-CH$_3$C$_6$H$_4$	−0.41
		p-C$_2$H$_5$C$_6$H$_4$	−0.41
p-OHCC$_6$H$_4$	−0.23	p-CH$_3$OC$_6$H$_4$	−0.45
(C$_6$H$_5$)$_2$CH	−0.28	p-(CH$_3$)$_2$NC$_6$H$_4$	−0.57

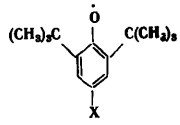
A two-electron wave ($E''_{1/2}$ = −1.4 V), which corresponds to the formation of a trianion, has been detected in the polarogram of radical (VI) in addition to the one-electron reduction wave. A similar wave has been observed in the polarographic reduction of the corresponding phenoxide. The existence of the trianion and its reversible conversion into the phenoxide ion have been demonstrated by ultraviolet spectroscopy and the intermediate formation of the radical dianion has been demonstrated by ESR.[46]

The values of $E'_{1/2}$ for 2,6-di-t-butyl-4-(p-X-phenyl)-phenoxy-radicals (Table 3) shift towards more negative potentials as the electron-donating properties of the substituent X become more pronounced and are satisfactorily correlated with the electrophilic constants σ^+ (r = 0.983). Thus, polarographic analysis shows that phenoxy-radicals are active electron acceptors and in reactions with nucleophilic agents are converted into phenoxides by

accepting one electron in a vacant orbital. Such reactions include primarily the thoroughly investigated reactions of stable phenoxy-radicals with alkali metals[48,49], phosphites[50,51], amines[2,52,53], organometallic compounds[54-57], and certain iodides[58-61]. A series of studies involving kinetic methods for the investigation of reactions of phenoxy-radicals have been made by Pokhodenko[2,49-51]. For example, he showed that the rate of reaction of triethylamine with phenoxy-radicals depends on the electron-accepting properties of the latter and that the reaction of the same phenoxy-radicals (III) with triethyl phosphite as a nucleophilic agent is much slower than that with triethylamine[50].

Comparison of the kinetic parameters for the reaction of triethylamine or diethylamine with a number of 2,6-di-t-butyl-4-(*p*-X-phenyl)phenoxy-radicals with the polarographic reduction potentials have shown that the reaction of phenoxy-radicals with tertiary amines proceeds only via the one-electron transfer mechanism (correlation of the reduction potentials of the radicals with kinetic parameters; Table 4), while in the reaction of phenoxy-radicals with secondary amines the transfer of one electron and the elimination of a hydrogen atom play a significant role simultaneously[62].

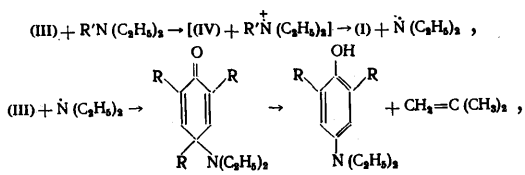
Table 4. Kinetic parameters of the re. on of the phenoxy-radicals

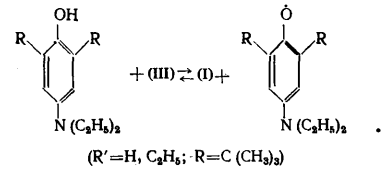


with amines.

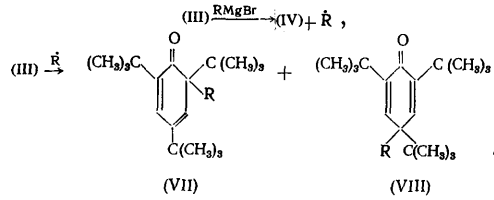
X	Triethylamine			Diethylamine		
	$10^5 k$, litre mole^{-1} s^{-1}	k_0, litre mole^{-1} s^{-1}	E_{act} ± 0.5, kcal mole^{-1}	$10^4 k_{10}$, litre mole^{-1} s^{-1}	k_0, litre mole^{-1} s^{-1}	E_{act} ± 0.5 kcal mole^{-1}
$C(CH_3)_3$	36.0	$2{,}8\cdot10^8$	12.8	9.0	$5{,}9\cdot10^5$	11.4
p-$CH_3C_6H_4$–	9,8	$3{,}7\cdot10^4$	10.7	3.8	$1{,}2\cdot10^5$	10.1
C_6H_5–	13.0	$1{,}3\cdot10^4$	10.1	10.6	$7{,}6\cdot10^4$	9.7
p-ClC_6H_4–	16.7	$7{,}3\cdot10^3$	9.5	12.5	$1{,}5\cdot10^5$	10.1
p-$CH_3OOCC_6H_4$–	25.0	$2{,}3\cdot10^3$	8.7	24.0	$4{,}0\cdot10^5$	10.3
p-$CH_3COC_6H_4$–	36.0	$3{,}9\cdot10^3$	8.8	19.6	$3{,}2\cdot10^5$	10.3

The main product of the reaction of phenoxy-radicals with amines is the corresponding phenol[62-64]. The formation of insignificant amounts of 4-*NN*-dialkylamino-2,6-di-t-butylphenoxy-radicals, detected by ESR, in the reaction of (III) with amines, shows that the interaction of the phenoxy-radical with the radical obtained from the amine takes place in the main reaction and that according to these data the overall reaction mechanism can be represented as follows:



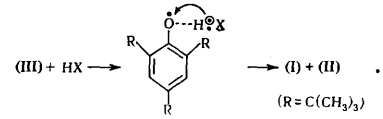


The reaction of phenoxy-radicals with organomagnesium compounds takes place almost instantaneously even at −70°C. The reaction with alkylmagnesium halides yields, apart from magnesium phenoxide, *gem*-dialkylcyclohexadienones (VII) and (VIII) owing to the interaction of the phenoxy-radicals present in excess with the alkyl radicals[57].

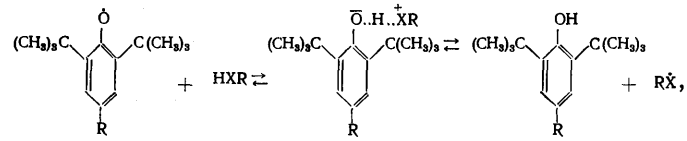


The formation of biphenyl was observed in a study of the reaction of (III) with phenyl-lithium[54] and phenylmagnesium bromide[56].

In recent years, reports have appeared in the literature in which dehydrogenation by phenoxy-radicals is regarded as involving the transfer of one electron in a complex[65-67]. This mechanism explains satisfactorily the dehydrogenation of inorganic acids by stable phenoxy-radicals[65,66,68,69], since the energy of the HX bonds in inorganic acids is as a rule higher than 100 kcal mole^{-1} [70] and therefore it is difficult to postulate the possibility of a direct elimination of a hydrogen atom from such a substrate by a phenoxy-radical:



Müller et al., who investigated a large number of reactions involving dehydrogenation by phenoxy-radicals, postulate the formation in the first stage of an ion pair complex in which one-electron transfer can take place[20]:



where X = heteroatom.

Among reactions of a similar type, the dehydrogenation of various phenolic compounds and amines by phenoxy-radicals has been most completely studied[71-76]. Although the investigators of these reactions in most cases supported the mechanism where atomic hydrogen is eliminated in the elementary step, nonetheless their experimental data fits satisfactorily the hypothesis of the one-electron transfer mechanism for the process.

4. STERICALLY HINDERED CYCLOHEXADIENONES

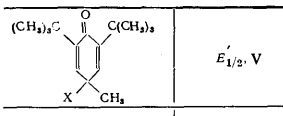
The factor which determines the reactivity of various cyclohexadienones (quinolide compounds) is the nature of the geminal substituents, which in many ways determines

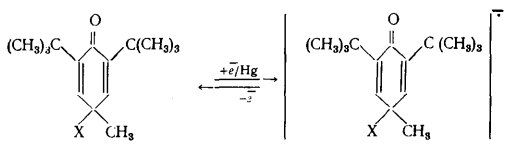
the specificity of the chemical behaviour of the molecule and in the first place its tendency to undergo reactions with a one-electron transfer (reactions with nucleophilic agents and metals and electrochemical reduction). The effect of the nature of the geminal substituents on similar process has been shown most distinctly in the polarographic reduction of quinolide compounds[77].

Electron affinity (the energy of the lowest vacant molecular orbital[78]) is usually satisfactorily correlated with the half-wave potential for the polarographic reduction of the quinolide compound in aprotic media. Therefore polarographic reduction data for quinolide compounds can be used as indices of the reactivity of these compounds in their interaction with the electron, which is the simplest nucleophilic agent.

The polarographic reduction of 4-alkyl-2,6-di-t-butyl-4-methyl-cyclohexa-2,5-dienones (VIII) and (IX) at a dropping mercury electrode in dimethylformamide solution (DMF) gives rise to a one-electron wave, the analysis of which indicates the reversibility of the process occurring in the reduction of compounds (VIII) and (IX) (Table 5).[77]

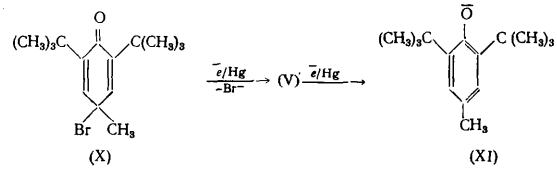
Table 5. Polarographic characteristics of quinolide compounds.

	$E'_{1/2}$, V	i_d, μA	α	$E''_{1/2}$, V	i_d, μA	α
Br	—0.31	1.0	1.0	—0.46	0.52	0.4
Cl	—1.13	3.05	0.9	—	—	—
NO_2	—1.30	3.13	0.8	—	—	—
OCH_3	—1.31	1.66	0.6	—2.20	0.36	0.8
OH	—1.59	1.44	0.2	—2.18	0.54	0.8
CH_3	—2.18	1.48	1.0	—	—	—
$C(CH_3)_3$	—2.24	1.82	1.0	—	—	—



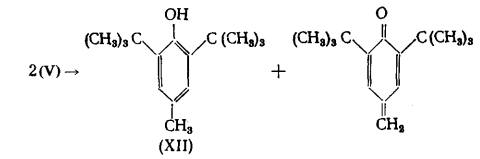
X=C(CH₃)₃ (VIII) X=C(CH₃)₃ (VIIIa)
X=CH₃ (IX) X=CH₃ (IXa)

The formation of the radical-anions (VIIIa) and (IXa) has been confirmed by ESR (the spectrum of the radical-anion consists of a 1:2:1 triplet, $a_{H(meta)}$ = 6.6 G).[79] The polarographic reduction of the quinobromide (X) gives rise to two polarographic waves:



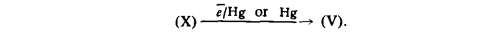
(X) (XI)

At the first half-wave potential ($E'_{\frac{1}{2}}$ = −0.31 V), the phenoxy-radical is formed instead of the corresponding radical-anion which indicates the dissociation of the C—Br bond in the electrochemical reduction process with formation of the phenoxy-radical and a bromide ion[77,79]. The second one-electron wave is due to the reduction of (V) and is irreversible. The limiting current of the second half-wave for the polarographic reduction of the quinobromide (X) was found to be lower than would be expected for a one-electron process and is probably related to the simultaneous disproportionation of the phenoxy-radical via the mechanism[80]:



(XII)

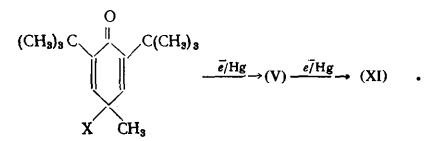
It is noteworthy that quinobromides react slowly with neutral mercury[48], forming phenoxy-radicals and this is why the limiting current for the polarographic reduction of the quinobromide (X) seems to be low, (i_d = 1 μA instead of i_d = 1.5 ± 0.2 μA for the one-electron process):



These two simultaneous processes involve the same mechanism but proceed at different rates. The initial stage is electron transfer in both cases.

The polarographic reduction of quinobromides, where the bromine atom is linked to a tertiary carbon atom, constitutes a specific example of the polarographic reduction of alkyl halides. Usually the electrochemical reduction of tertiary alkyl halides has a low transfer coefficient, since the reduction of these compounds has a S_N1-like mechanism[81]. In the polarographic reduction of compound (X), the transfer coefficient α = 1, which may indicate electron transfer from the cathode directly to the vacant orbital of the bromine atom in the molecule of (X).

The quinochloride (XIII) and the 4-nitrocyclohexadienone (XIV) interact with an electron at more negative potentials than (X) and (V). In these cases, one two-electron wave due to the stage-by-stage one-electron reduction is observed in the polarographic reduction process[77]:

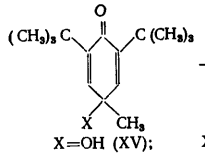


X=Cl (XIII); X=NO₂ (XIV)

The intermediate formation of a phenoxy-radical in a similar electrochemical reaction has been confirmed by ESR.[82]

Analysis of the results of the polarographic reduction of hydroquinone (XV) and its methyl ether (XVI) showed that the mechanism of their reduction differs from that described above. The difference consists primarily in the fact that the main (first) polarographic wave corresponds to a one-electron process. This rules out the intermediate formation of a phenoxy-radical as the main reaction product, since the reduction potentials of (XV) and (XVI) are more negative than the reduction potentials of (V) and other phenoxy-radicals[46]. In addition, the transfer coefficient in the polarographic reduction of (XV) and (XVI) differs markedly from the transfer coefficient for the first polarographic wave of (X), probably because of the decrease of the transfer of a fractional electronic charge in the transition state in the reduction of (XV) and (XVI). It is most likely that electron capture by hydroquinone (XV) or its ether (XVI) leads to the formation of

the corresponding phenoxide (with simultaneous elimination of the radicals $\dot{O}H$ or $\dot{O}CH_3$) and not of a phenoxy-radical and an anion:



$\xrightarrow{\bar{e}/Hg}$ (XI) + $\dot{X}$.

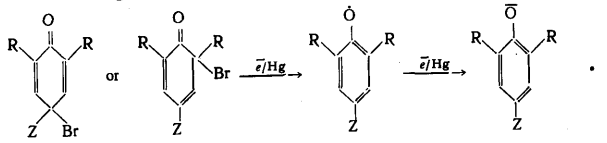
X=OH (XV); X=OCH_3 (XVI)

According to this mechanism of the polarographic reduction of (XV) and (XVI), the formation of a second wave ($E''_{1/2} \simeq -2.19$ V), the limiting current of which is smaller almost by a factor of three than that of the first wave, may be attributed to the reduction of substances produced from the solvent when it interacts with the radicals $\dot{O}H$ and $\dot{O}CH_3$ (Table 5).

Table 6. Polarographic characteristics of quinobromides.

Position of bromine atom	Z	$E'_{1/2}$, V	i_d, μA	α	$E''_{1/2}$, V	i_d, μA	α
4	CH_2Br	—0.24	1.0	1.0	—0.39	1.0	0.9
2	CHO	—0.13	1.7	0.4	—0.42	1.4	0.4
2	$COCH_3$	—0.11	1.4	0.7	—0.47	1.5	0.4
2	CN	—0.01	1.0	0.6	—0.[illegible]	1.1	0.4
2	Br	0.05	0.9	0.8	—0.[illegible]	1.5	0.8
2	NO_2	0.13	1.0	0.3	—0.29	1.0	0.7

The introduction of a second functional group into quinolide compounds has a significant influence on the results of their polarographic reduction. Interesting data were obtained in the reduction of quinobromides with various substituents in the 4-position[77] (Table 6). In such cases, two one-electron waves are produced, corresponding to the individual stages of the reduction process occurring at different potentials. The first stage proceeds with transfer of one electron from the cathode to the quinobromide molecule, the reaction being accompanied by the formation of a phenoxy-radical and a bromide ion. The second stage is the reduction of the phenoxy-radical:



(Z=CH_3, CH_2Br; Br; CHO; $COCH_3$; CN; NO_2 R=C $(CH_3)_3$)

The electron affinity (the first half-wave potential) of substituted quinobromide compounds increases with increase of the negative inductive effect of the substituent.

The limiting current depends significantly on the nature of the substituent in the quinobromides and on the properties of the intermediate phenoxy-radicals. The dependence of the transfer coefficient on the solvent for quinobromide compounds indicate a significant contribution of the electronic effects of these substituents to the transition state. However, despite the fact that in the polarographic reduction of many quinobromides compounds the transfer coefficient changes and in addition the electrochemical reaction is accompanied by a chemical reaction, the calculated first half-wave potential for the polarographic reduction of quinobromides compounds are satisfactorily correlated with Taft's σ constants ($r = 0.952$). The presence of such correlation may serve as confirmation of the generality of the mechanism of the electrochemical reduction of quinobromide compounds. Probably the electron cloud of the bromine atom shifts under the influence of electronegative substituents, the atom requiring as a result a positive charge. In the electrochemical reduction, an electron is transferred to a vacant bromine orbital and more readily the higher the partial positive charge on the bromine atom. The elimination of a bromide ion with a formal homolytic dissociation of the C—Br bond in the quinolide compound molecule is a consequence of the electron transfer. The mechanism proposed for the interaction of quinolide compounds with an electron is satisfactorily consistent with experimental polarographic data and is fully consistent with the reactions of the various quinolide compounds involving one-electron transfer.

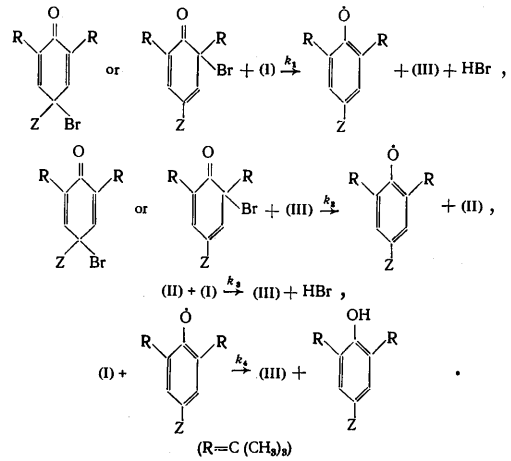
It has been found from kinetic data[83] for the reaction of (III) with hydrogen halides and the phenolic OH and halogen bond energies that $E_{C-Br} = 16.6 \pm 3$ kcal mole^{-1} and $E_{C-Cl} = 32.9 \pm 3$ kcal mole^{-1} for quinohalides:

2(III) + HX $\rightleftarrows$ (I) + (II) .

The unusually low bond energies between the halogen atom and a carbon atom of the six-membered ring of cyclohexadienones make quinobromides and quinochlorides compounds (as well as 4-nitrocyclohexadienones) thermally unstable, the compounds decomposing even at temperatures below 100°C with formation of phenoxy-radicals[58,84,85]. For this reason, certain quinobromides rearrange spontaneously on standing at room temperature to 3,5-di-alkyl-4-hydroxybenzyl bromides[85,86]. The reaction involves the intermediate formation of a phenoxy-radical.

A kinetic study of the interaction of various quinobromides with (III) has shown that the activation energy increases with the electronegativity of the substituent in the quinobromide[87]. This relation indicates an increase of the resistance of the C—Br bond to homolytic dissociation in the series of bromocyclohexadienones with increase of the electronegativity of the substituent (Table 7).

An analogous relation has been obtained in a kinetic study of the reaction of the same quinobromides with (I),[14] although the reaction does not stop in the first stage. In the presence of an excess of the quinobromide, the four reactions represented in the scheme below can occur:



(R=C $(CH_3)_3$)

In the reaction with a quinobromide containing the nitro-group (Z = NO_2), $k_1 = 7 \times 10^{-6}$, $k_2 = 8 \times 10^{-2}$, $k_3 = 5 \times 10^{-7}$, $k_4 = 10^3$ litre mole^{-1} s^{-1}.

gem-Dialkylcyclohexadienones, hydroquinones, and their ethers are as a rule more thermostable and therefore the bond energy between the geminal substituent and a carbon atom in the six-membered ring presumably differs little from the C—C or COR bond energy in the usual organic compounds. Consequently the properties of quinolide compounds change sharply on passing from quinobromide, quinochloride, and 4-nitrocyclohexadienones to other cyclohexadienones. Their behaviour in reactions with one-electron transfer is determined by the lower electron affinity of the geminal substituent and the higher stability of the bond linking it. Thus the reaction of *gem*-dialkylcyclohexadienones with metallic potassium in tetrahydrofuran yields a stable radical-anion[79]:

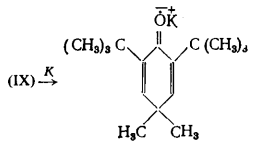
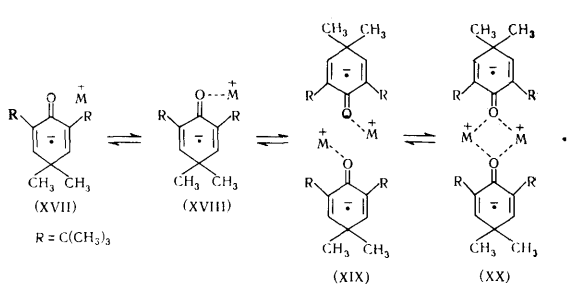


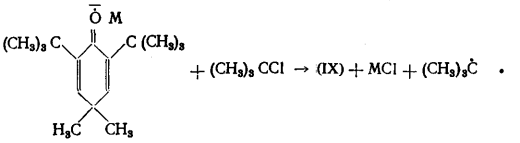
Table 7. Activation energies for the reaction of (III) with bromocyclohexadienones.

Z	Position of bromine atom	$E_{act} \pm 1$, kcal mole^{-1}	Z	Position of bromine atom	$E_{act} \pm 1$, kcal mole^{-1}
CH_3	4	4.2	CHO	2	13.1
CH_2Br	4	7.0	Br	2	13.7
CN	2	12.4	NO_2	2	13.2

The structure of the paramagnetic species obtained in the interaction of *gem*-dialkylcyclohexadienones with alkali metals depends significantly on the nature of the metal, the solvent, and temperature. A detailed analysis of the ESR spectra of the radical-anions from the cyclohexadienone (VIII), obtained in different media, made it possible to deduce the chain of reactions involving these radical-anions when the solvating capacity of the solvent is reduced[88]:



The ion pair (XVII) separated by solvent molecules is converted into a contact ion pair (XVIII) which is subsequently converted into the paramagnetic dimer (XIX) separated by solvent molecules. In turn, the dimer (XIX) is converted into a contact dimer (XX). It has been shown[88-91] that the cations are desolvated in the course of these transformations. It has been established for the reaction of the above radical-anions with t-butyl chloride[92], the rate-limiting stage of which is apparently the transfer of one electron from the radical-anion to the alkyl halide, that the reactivity of the radical-anion increases with decrease of the degree of desolvation of the cation:

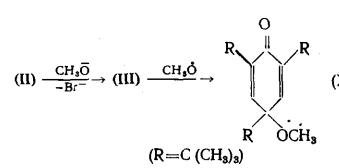


The activation energy for this reaction is higher in solvating media and increases in the series of cations TBA§ < Na < Li (Table 8). The formation of metal chlorides is accompanied by the disruption of the solvation shell of the cation and presumably the differences between the activation energies are related to the difference between the heats of solvation of the corresponding cations. Indeed, the difference between the activation energies in THF and in ethyl ether for the reaction of t-butyl chloride with the radical-anion of 2,6-di-t-butyl-4,4-dimethylcyclohexa-2,5-dienone, with Na^+ and Li^+ as the cations, is the same as the difference between the heats of solvation of these cations by the solvent molecules, calculated by analysing the ESR spectra of the radical-anions[88-92].

Table 8. Kinetic parameters of the reaction of t-butyl chloride with the radical anion of the metal derivative of 2,6-di-t-butyl-4,4-dimethylcyclohexa-2,5-dienone.

Cation	Solvent	$10^3 k$ (0°), litre mole^{-1} s^{-1}	$10^{-10} k_0$, kcal mole^{-1} s^{-1}	$E_{act} \pm 0.5$, kcal mole^{-1}
Sodium	DME	0.79	0.4	15.6
Sodium	THF	1.50	2.4	16.3
Sodium	Ethyl ether	7.00	0.1	13.5
Lithium	THF	0.09	260	20.4
Lithium	Ethyl ether	0.40	0.04	14.7
TBA	THF	$5 \cdot 10^2$	0.1	11.3

All the data quoted above show that, among quinolides of different types, the quinobromides should enter most readily into chemical reactions involving the transfer of one electron. Indeed, reactions of this type proved to be extremely characteristic of such compounds. The majority of known reactions of quinobromides, for which an ionic mechanism has been postulated earlier, probably proceed via the scheme under consideration. For example, 2,4,6-tri-t-butyl-4-methoxyhexa-2,5-dienone (XXI) was obtained in the reaction between compound (II) and alkaline solutions of methanol and the appearance of a blue colour in the course of the reaction was noted[48]. Only later was it shown that the blue colour is due to the appearance of the phenoxy-radical (III):[93]



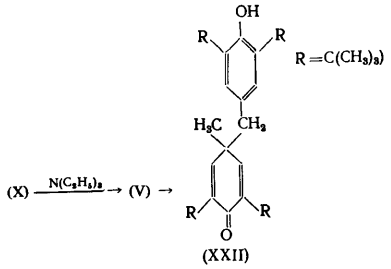
The phenoxy-radical (X) is also formed when compound (II) interacts with amines[93-96], organomagnesium compounds[97], alkyl phosphites[50,51], triphenylphosphine[98], phenoxides[36-38,48,99], and various metals[48,49,54,58].

§ TBA = tetrabutylammonium.

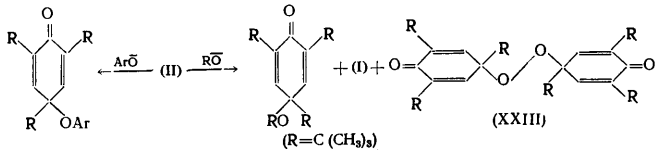
Certain metals, such as mercury, silver, copper and zinc, are readily oxidised on reacting with quinobromides and only the phenoxy-radical is obtained from compound (II).[48] The radical (III) is also formed initially by the reaction of compound (II) with alkali metal and is capable of further reaction with these electron donors, so that the final product is the corresponding phenoxide[48,49]:

$$(III) \xleftarrow[95\%]{Ag} (II) \xrightarrow{K} (III) \xrightarrow{K} (IV)\ .$$

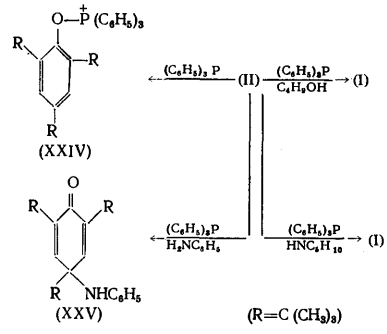
The nature of the products of the reaction of quinobromides with nucleophilic agents depends significantly on the nature of the substituents in the quinobromide molecule and on the stability of the phenoxy-radicals formed. If unstable phenoxy-radicals are obtained in the reaction of quinobromides with nucleophilic agents, then a considerable amount of products of the recombination and disproportionation of the phenoxy-radicals are present in the reaction mixture[100-103]. Therefore reaction conditions have a significant influence on the results of the interaction of the same reactants. For example, at room temperature the quinobromide (X) reacts very slowly with triethylamine and therefore it has been stated[104] that it is stable in relation to triethylamine. However, at an elevated temperature the reaction of (X) with triethylamine and certain other amines is fairly vigorous and involves the formation of the quinolide compound (XXII) as the main product[95]:



The reaction of compound (II) with phenoxides leads to the formation of hydroquinone ethers in almost quantitative yields[105,106], but in the reaction with alkoxides (particularly at a reduced temperature) compound (I) and the quinolide peroxide (XXIII) are also formed in considerable amounts owing to the interaction of the radical (III) with oxygen[93]:

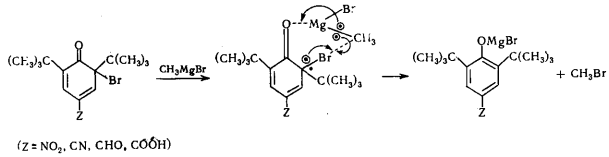


It is interesting that the hydroquinone ether (XVI) is also produced as a result of the interaction of the quinobromide (X) with methanol[107]. The effect of the solvent and other factors have been investigated in the reaction of compound (II) with triphenylphosphine[98]. The radical (III) is also formed initially in this reaction and then reacts further with formation of the substances indicated below:



When the reaction is carried out in the absence of a solvent, the triphenylphosphine derivatives of 2,4,6-tri-t-butylphenol (XXIV) is formed, in solution in s-butyl alcohol or piperidine the product is compound (I), and in the presence of aniline the quinamine (XXV) is isolated. There is now no doubt about the radical mechanism of the reaction of quinobromides with alkyl phosphites[50,51], although initially an ionic mechanism was proposed for this reaction[108,109].

Interesting data were obtained also in a study of the reaction of quinobromides with organomagnesium compounds. Firstly, it was shown in this reaction that organomagnesium compounds can take part in reactions involving the transfer of one electron and, secondly, it was possible to elucidate the effect of the nature of the substituents in the quinobromide molecule on the properties of the bromine atom in chemical reactions involving the transfer of one electron. It was found that, depending on the nature of the substituents in the quinobromides, their reaction with a Grignard reagent results in the formation of either a magnesium halide and a phenoxy-radical or of an alkyl bromide and the corresponding phenoxide ion[110]. The second reaction pathway is possible for quinobromides containing electronegative substituents. Such quinobromides usually have an *ortho*-quinolide bond system[111]. It is noteworthy that in this case electronegative substituents enhance the electron affinity of the quinobromides to an even greater extent (see, for example, the data for their polarographic reduction in Table 6). To account for this reaction pathway, it has been suggested that the C—Br bond in quinobromides becomes more heteropolar under the influence of electronegative substituents than the corresponding bond in analogous compounds with alkyl substituents only[112]. Therefore, the transfer of one electron in the reaction of the above quinobromides with a Grignard reagent make more favourable the formation of a phenoxide ion (stabilised by internal conjugation) with the formal elimination of bromine in the form of a radical rather than the formation of a phenoxy-radical:



The same mechanism has been proposed also for the reaction of certain α-bromoketones with metal carbonyls and the formation of the bromine radical was confirmed experimentally[113]. It is interesting that an analogous reaction mechanism holds also in the interaction of organomagnesium compounds with cyclohexadienones in which one of the geminal substituents is the OH or OCH_3 group. These reactions yield only phenoxides[114]. Thus butyl methyl ether was isolated in addition to compound (XII) in the reaction of (XVI) with butylmagnesium bromide:

$$(XVI) + C_4H_9MgBr \rightarrow (XII) + C_4H_9OCH_3 .$$

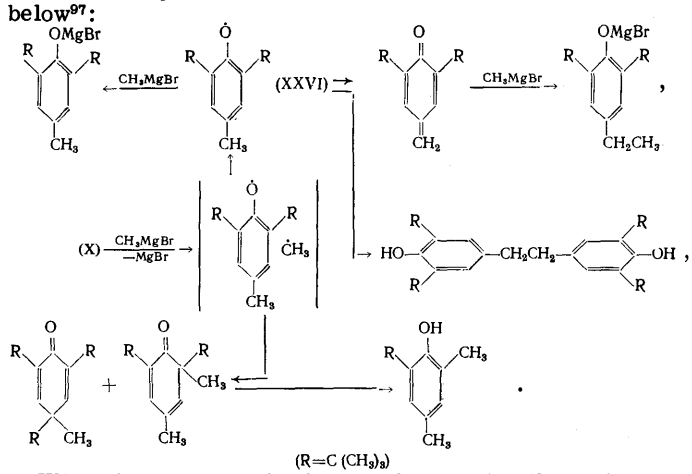
gem-Dialkylcyclohexadienones are stable also in the presence of an excess of the Grignard reagent and form radical-anions, which are reconverted into quinolide compounds in the presence of acid.

In a study of the above reactions of quinobromides with electron-donating agents accompanied by the formation of two radicals and the elimination of a bromide ion, account must undoubtedly be taken of the formation of a biradical "cage" and of the effects of its properties on the further reaction pathway. Hypotheses concerning the "cage" effect in radical reactions, in particular in reactions with one-electron transfer, are now being developed and have been generally accepted[115-117]. Depending on the properties of the "cage", determined by various factors, two processes are possible under these conditions. Firstly, radicals forming the "cage" may recombine within the "cage", yielding the expected reaction product. Secondly, on overcoming the solvation shell the radicals become kinetically independent species and as a rule give rise to a large number of side products in addition to the main reaction product. Usually these two processes are competitive. In the vast majority of cases, they take place simultaneously in reactions of quinolide compounds with one electron transfer, but their probabilities are different (depending on the nature of the nucleophilic agent, the solvent, temperature, and even the order in which the reactants are added). For example, the order of addition of the reactants in the reaction of quinobromides of types (II) or (X) with a Grignard reagent has a very significant influence on the results of the reaction.

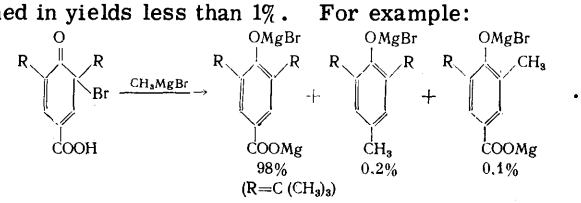
Table 9. Rate constants for the reaction of (X) with amines at 40°C.[118]

Amine	Solvent	10^3k, litre mole^{-1} min^{-1}	Amine	Solvent	10^3k, litre mole^{-1} min^{-1}
Morpholine	CCl_4	6.1	Di-isopropyl amine	Benzene	2.3
ditto	Heptane	5.5	t-butylamine	ditto	0.4
»	Benzene	6.1	Diethylamine	»	19.0
»	THF	15.0	Triethylamine	»	45.0
»	Dioxan	18.0	Piperidine	»	43.0

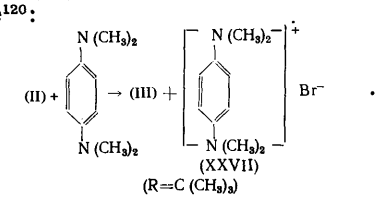
When an ethereal solution of (X) is added to a Grignard reagent, the phenoxy-radical (XXVI) is mainly formed and is consumed both in the disproportionation reaction and in the interaction with an excess of the organomagnesium compound. When the reactants are added in the opposite order, up to 20–30% of *ortho*- and *para-gem*-dialkylcyclohexadienones is formed in addition to compound (XXVI) and the products of its further reactions, part of the cyclohexadienones being formed as a result of the recombination of radicals within the "cage". The overall result of the secondary reactions of (X) with methylmagnesium bromide is the formation of seven different compounds via the mechanisms illustrated below[97]:



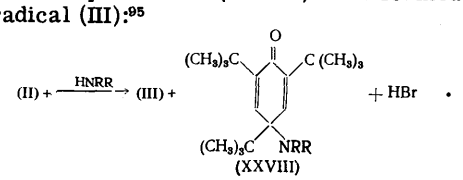
When the reaction of a Grignard reagent with a quinobromide containing electronegative substituents is carried out, the order of addition of the reactants no longer has a significant influence on the nature of the reaction products, since the transfer of one electron results in the preferential formation of the corresponding phenoxide and only a slight amount of phenoxy-radicals, which have been detected by ESR.[110] Therefore the products of the recombination of these phenoxy-radicals with alkyl radicals are formed in yields less than 1%. For example:



The effect of the "cage" on the nature of the products has been investigated also in the reaction of quinobromides with amines[118-120]. In a study of the reaction of (II) with tetramethyl-*p*-phenylenediamine by ESR, it was shown that the formation of (III) and the amine radical-cation (XXVII) is quantitative[120]:



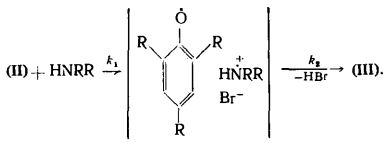
On the other hand, in the reaction of (II) with morpholine and piperidine products of the substitution of bromine by an amine—the quinamines (XXVIII)—are formed in addition to the radical (III):[95]



It follows from the kinetic data obtained for the consumption of the initial quinobromide and the accumulation of the phenoxy-radicals that the reaction is bimolecular and is of first order with respect to the quinobromide and the amine. The rate constant for the reaction of (X) with morpholine increases only slightly with the solvating capacity of the solvent, but the rate of the reaction of the same quinobromide depends significantly on the nature of the amine (Table 9). It has been shown for the reaction of (X) with

diethylamine and its *N*-deuteriated analogue that there is no isotopic effect in this process.[118]

On the hypothesis of one-electron transfer, the mechanism of the initial reaction step can be represented as follows:



The amine radical-cation formed in this step readily split off a proton and is converted into an amine radical. The latter either recombines in the "cage" with a phenoxy-radical, which leads to the main reaction product (quinamine), or emerges from the "cage" to give other reaction products. Its liberation from the "cage" is accompanied by the accumulation of phenoxy-radicals. Bearing in mind that only phenoxy-radicals emerging from the "cage" with a probability φ are detected, according to the proposed mechanism the rate of accumulation of the amine hydrobromide and phenoxy-radicals can be formulated as follows: $d[\dot{PhO}]/dt = k_2[PhOBr]$, $d[HBr]/dt = k_1[PhOBr]$, and $k_2 = \varphi k_1$, where [PhOBr] is the concentration of the quinobromide, [PhȮ] the concentration of phenoxy-radicals, [HBr] the concentration of hydrogen bromide, and φ the fraction of radicals released from the "cage".

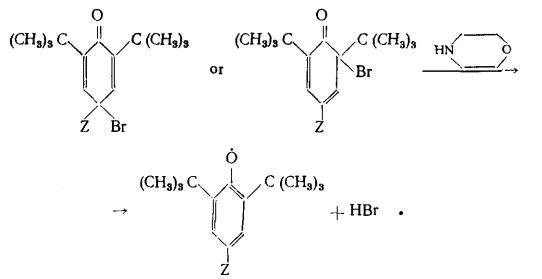
Table 10. Kinetic parameters of the reaction of (II) with amines and yields of quinamines.

Method	Amine	k_1 (40°), litre mole^{-1} min^{-1}	$10^4 k_2$ (40°) litre mole^{-1} min^{-1}	$10^{-8}k_0$, litre mole^{-1} min^{-1}	$1-\varphi$*	Yield of quinamine, %
Accumulation of HBr	Morpholine	28	—	0.8	0.93	85
Accumulation of (III)	Morpholine	—	1.9	0.72		
Accumulation of HBr	Piperidine	18	—	7.0	0.33	12
Accumulation of (III)	Piperidine	—	12	12.0		

* $1 - \varphi$ is the fraction of radicals (III) recombining within the "cage".

The kinetics of the accumulation of both hydrogen bromide (amine hydrobromide) and of radicals (III) have been investigated for the reaction of compound (II) with morpholine and piperidine[118]. The fraction of radicals released from the "cage" was calculated from the constants obtained for the formation of the "cage" and the liberation of radicals from the "cage" (Table 10). The kinetic data for this reaction were found to be in good agreement with the corresponding experimental results. Thus the reaction of (II) with morpholine yields 85% of the quinamine [2,4,6-tri-t-butyl-4-(*N*-morpholinyl)hexa-2,5-dienone]. Analysis of the kinetics of this reaction showed that the yield of the quinamine is 93%. On the other hand in the reaction of (II) with piperidine, the main pathway involves the liberation of radicals from the "cage" and therefore the rate constants found by the two methods agreed to within 30%. These results may be regarded as one of the pieces of evidence in support of the proposed mechanism involving the transfer of one electron in the elementary step of the interaction between two neutral substances.

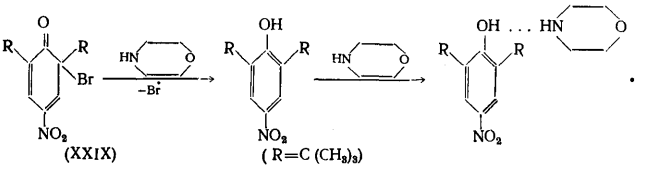
Additional data confirming the hypothesis of the one-electron stage were obtained in a study of the kinetics of the reaction of a number of quinobromides with an amine; depending on the nature of the substituents in the quinobromide molecule, the number of phenoxy-radicals liberated from the "cage" varied within wide limits[119]. Nevertheless the logarithms of the rate constants in this reaction series fit with a satisfactory correlation (r = 0.984) the relation with the first half-wave potential in the polarographic reduction of quinobromides. A similar relation, with a correlation coefficient r = 0.993 was established between the logarithms of the rate constants for the reaction of morpholine with quinobromides and Taft's constants σ for the substituents in the quinobromide molecule. It follows from these results that the effect of substituents in the reaction series investigated mainly involves an inductive mechanism:



(Z=CH$_3$; C$_2$H$_5$; C(CH$_3$)$_3$; CH$_2$Br; COCH$_3$; Br)

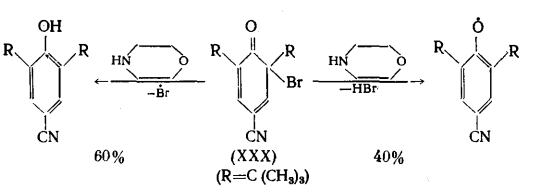
When the reaction of morpholine with quinobromides containing functional substituents was carried out, the corresponding quinamines could not be isolated, which is evidence of the preferential liberation of radicals from the "cage" under these conditions[119]. The phenoxy-radicals formed in this instance are consumed mainly via two pathways; in the reaction with the amine with formation of the phenoxide anion and in the disproportionation reaction[100].

It is noteworthy that the reaction of morpholine with the quinobromides (XXIX) and (XXX), where the substituents are nitro- and cyano-group, takes place somewhat differently. For example, in the reaction of morpholine with (XXIX) (Z = NO$_2$), the formation of hydrogen bromide and of the phenoxy-radical is not observed and the reaction yields only 2,6-di-t-butyl-4-nitrophenol which forms a complex in the presence of an excess of the amine[119]:



(XXIX) (R=C(CH$_3$)$_3$)

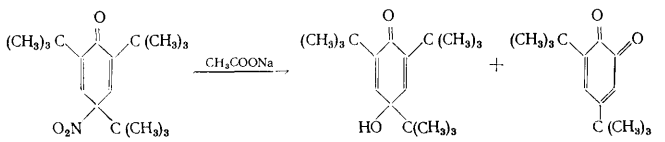
About 60% of hydrogen bromide is formed in the reaction of morpholine with (XXX) (Z = CN), which is evidence of the occurrence of approximately equivalent pathways in the decomposition of the hypothetical radical-anion with formation of both the bromide ion and atomic bromine:



60% (XXX) (R=C(CH$_3$)$_3$) 40%

These results are satisfactorily consistent with the behaviour of the above cyclohexadienones in their reactions with organomagnesium compounds[112].

The general characteristics of the reactions of quinochloride compounds and 4-nitrocyclohexadienones with nucleophilic agents remain the same as those of the reactions with quinobromide compounds, but these types of quinolides have been much less thoroughly investigated. Thus, it is known that the reaction of quinochlorides and 4-nitrocyclohexadienones with metals[48,49,54], phosphites[50,51], amines[2], and organometallic compounds[114] results in the formation of phenoxy-radicals. When potassium iodide acts on quinochlorides, free iodine is liberated[121] while in the reaction of 4-nitrocyclohexadienones and quinochlorides in aqueous alcoholic solutions of alkali, phenoxy-radicals are also formed initially[49]. The final product of the reaction of 2,4,6-tri-t-butyl-4-nitrocyclohexa-2,5-dienone with alkali (in aqueous acetone solution) is the corresponding hydroquinone[60]. It is interesting that the analogous reaction involving the replacement of the nitro-group by a hydroxyl takes place also under the influence of sodium acetate in acetic acid solution[60,122,123]:



We believe that the mechanism proposed for this reaction and involving nucleophilic substitution[122] is doubtful, since the hydrolysis of 4-nitrocyclohexadienones results in the formation, apart from the hydroquinones indicated above, of products characteristic of reactions in an alkaline medium of the corresponding phenoxy-radicals; quinones, 3,5-di-t-butyl-4-hydroxybenzaldehyde, and others[122,123] (see also Refs. 33–42).

Hydroquinones, their ethers, and *gem*-dialkylcyclohexadienones are as a rule resistant to the reaction of the majority of nucleophilic agents and only active electron donors such as alkali metals (or others in electrochemical reduction) can react with these quinolides to form radical-anions[79]. Examples of reactions of hydroquinones involving the carbonyl group are also known. Thus the reaction of 2,6-di-t-butyl-4-hydroxy-4-methylcyclohexa-2,5-dienone with organolithium compounds results in the formation of the corresponding cyclohexadienediols[124].

---o0o---

The reactions of sterically hindered phenols and their derivatives discussed above are in many cases typical for substances of this type and probably involve one-electron transfer in the elementary step. Quinobromide compounds, which form either phenoxy-radicals or the corresponding phenoxides after the addition of the electron depending on the structure, are of greatest interest for the investigation of various aspects of the problem under consideration. This makes it possible to separate the various stages in processes involving one-electron transfer.

REFERENCES

1. M.B. Neiman, Yu.G. Mamedova, P.L. Blenke, and A.L. Buchachenko, Dokl. Akad. Nauk SSSR, 144, 392 (1962).
2. V.G. Pokhodenko and N.N. Kalibabchuk, Teor. Eksper. Khim., 6, 124 (1970).
3. K. Ingold, Chem. Rev., 61, 563 (1961).
4. J. Howard and K. Ingold, Canad. J. Chem., 40, 1857 (1962).
5. E.G. Denisov and N.M. Emanuel', Uspekhi. Khim., 27, 365 (1958).
6. V.V. Ershov and A.A. Volod'kin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 2015 (1962).
7. G.A. Zlobina and V.A. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 1666 (1964).
8. V.V. Ershov, Doctoral Thesis, Institute of Organic Chemistry of the USSR Academy of Sciences, Moscow, 1965.
9. A.M. Vasserman, A.L. Buchachenko, G.A. Nikiforov, V.V. Ershov, and M.A. Neiman, Zhur. Fiz. Khim., 41, 705 (1967) [Russ. J. Phys. Chem., No. 3 (1967)].
10. N. Hash, J. Chem. Soc., 2375 (1953).
11. G. Coppinger, J. Amer. Chem. Soc., 86, 4385 (1964).
12. R. Bacon and O. Stewart, Chem. Comm., 977 (1967).
13. A.I. Prokof'ev, S.P. Solodovnikov, A.A. Volod'kin, and V.V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 174 (1971).
14. A.A. Volod'kin, V.V. Ershov, A.I. Prokof'ev, S.P. Solodovnikov, and D.Kh. Rasuleva, Izv. Akad. Nauk SSSR, Ser. Khim., 859 (1971).
15. A.I. Prokof'ev, S.P. Solodovnikov, A.A. Volod'kin, V.V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 1333 (1971).
16. B. Smith, U. Persmark, and E. Edman, Acta Chem. Scand., 17, 709 (1963).
17. C. Cook, C. Depatie, and E. English, J. Org. Chem., 24, 1356 (1959).
18. R. Kreilick and S. Weissman, J. Amer. Chem. Soc., 84, 306 (1962).
19. R. Kreilick and S. Weissman, J. Amer. Chem. Soc., 88, 2645 (1966).
20. E. Müller, R. Mayer, B. Narr, A. Schick, and K. Scheffler, Annalen, 645, 1 (1961).
21. A. Suttie, Tetrahedron Letters, 953 (1969).
22. V. Parker and A. Rolan, J. Electroanal. Chem. Interfacial Electrochem., 30, 502 (1971).
23. A. Rolan, J. Chem. Soc. (D), 1643 (1971).
24. B.I. Shapiro, L.V. Okhlobystina, V.M. Khutoretskii, A.V. Fainzil'berg, and Ya.K. Syrkin, Dokl. Akad. Nauk SSSR, 190, 151 (1970).
25. K.A. Bilevich, N.N. Bubnov, O.Yu. Okhlobystin, and N.G. Radzhabov, Dokl. Akad. Nauk SSSR, 191, 119 (1970).
26. T. Bruice, M. Gregory, and S. Walters, J. Amer. Chem. Soc., 90, 1612 (1968).
27. K.A. Bilevich, N.N. Bubnov, B. Ya. Medvedev, O.Yu. Okhlobystin, and L.V. Ermanson, Dokl. Akad. Nauk SSSR, 193, 583 (1970).
28. A. Bikel and H. Gersmann, Proc. Chem. Soc., 231 (1957).
29. J. Conradi and G. McLaren, J. Amer. Chem. Soc., 82, 4745 (1960).
30. K. Ley, Angew. Chem., 70, 74 (1958).
31. E. Müller and E. Schmidt, Chem. Ber., 97, 2614 (1964).
32. M. Pianka, J. Chem. Soc. (C), 2618 (1967).
33. M.P. Ponomarchuk, L.F. Kasukhin, and V.D. Pokhodenko, Zhur. Obshch. Khim., 41, 43 (1971).
34. K.A. Bilevich, N.N. Bubnov, O.Yu. Okhlobystin, and N.G. Radzhabov, Izv. Akad. Nauk SSSR, Ser. Khim., 1811 (1971).

35. K. A. Bilevich, N. N. Bubnov, O. Yu. Okhlobystin, and N. G. Radzhabov, Izv. Akad. Nauk SSSR, Ser. Khim., 2062 (1971).
36. N. N. Bubnov, S. G. Kukes, A. I. Prokof'ev, C. P. Solodovnikov, A. A. Volod'kin, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 2094 (1972).
37. S. G. Kukes, N. N. Bubnov, A. I. Prokof'ev, S. P. Solodovnikov, A. A. Volod'kin, G. A. Nikiforov, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 184 (1973).
38. S. G. Kukes, N. N. Bubnov, A. I. Prokof'ev, S. P. Solodovnikov, A. A. Volod'kin, G. A. Nikiforov, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 186 (1973).
39. L. M. Strigun, L. S. Vartanyan, and N. M. Emanuel', Uspekhi. Khim., 37, 969 (1968) [Russ. Chem. Rev., No. 6 (1968)].
40. L. M. Strigun, L. S. Vartanyan, A. A. Volod'kin, A. I. Prokof'ev, and N. M. Emanuel', Izv. Akad. Nauk SSSR, Ser. Khim., 2242 (1968).
41. V. D. Pokhodenko and N. N. Kalibabchuk, Zhur. Org. Khim., 5, 1413 (1969).
42. J. Pilar, L. Buben, and J. Pospisil, Tetrahedron Letters, 4203 (1968).
43. H. Gersmann and A. Bickel, J. Chem. Soc., 2356 (1962).
44. M. Kharasch and B. Joshi, J. Org. Chem., 22, 1439 (1957).
45. A. Rieker, P. Niederer, and H. Stegmann, Tetrahedron Letters, 3873 (1971).
46. A. I. Prokof'ev, S. P. Solodovnikov, G. A. Nikiforov, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 324 (1971).
47. I. T. Ioffe, A. I. Prokof'ev, S. P. Solodovnikov, A. A. Volod'kin, G. A. Nikiforov, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 2844 (1971).
48. E. Müller, K. Ley, and W. Kiedaisch, Chem. Ber., 87, 1605 (1954).
49. V. D. Pokhodenko and N. N. Kalibabchuk, Zhur. Org. Khim., 5, 1794 (1969).
50. N. N. Kalibabchuk, D. V. Saidul, and V. D. Pokhodenko, Zhur. Obshch. Khim., 39, 2140 (1969).
51. N. N. Kalibabchuk, L. M. Golubenkova, V. D. Pokhodenko, Zhur. Obshch. Khim., 41, 2205 (1971).
52. V. D. Pokhodenko and V. A. Bidzilya, Teor. Eksper. Khim., 2, 691 (1966).
53. E. Müller and K. Ley, Z. Naturforsch., 8b, 694 (1953).
54. E. Müller and K. Ley, Chem. Ber., 87, 922 (1954).
55. A. Rieker and E. Müller, Z. Naturforsch., 17b, 718 (1962).
56. E. Müller, P. Ziemek, and A. Rieker, Tetrahedron Letters, 207 (1964).
57. V. V. Ershov, A. A. Volod'kin, and M. V. Tarkhanova, Izv. Akad. Nauk SSSR, Ser. Khim., 2470 (1967).
58. C. Cook and R. Woodworth, J. Amer. Chem. Soc., 75, 6242 (1953).
59. E. Müller, A. Schick, and K. Scheffler, Chem. Ber., 92, 474 (1959).
60. E. Müller and K. Ley, Chem. Ber., 88, 601 (1955).
61. E. Müller, A. Rieker, K. Ley, R. Mayer, and K. Scheffler, Chem. Ber., 92, 2278 (1959).
62. S. G. Kukes, N. N. Bubnov, A. I. Prokof'ev, S. P. Solodovnikov, I. B. Khristman, A. A. Volod'kin, G. A. Nikiforov, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 944 (1972).
63. G. A. Razuvaev, G. A. Aabakumov, and E. S. Klimov, Dokl. Akad. Nauk SSSR, 205, 1093 (1972).
64. W. D. Pokhodenko, N. N. Kalibabtschuk, and W. A. Khizny, Annalen, 743, 192 (1971).
65. K. Dimroth, W. Umbach, and H. Thomas, Chem. Ber., 100, 132 (1967).
66. V. A. Khizhnyi and V. D. Pokhodenko, Zhur. Org. Khim., 5, 2189 (1969).
67. K. Dimroth, F. Kalk, and G. Neubauer, Chem. Ber., 90, 2058 (1957).
68. E. Müller, K. Ley, and W. Kiedaisch, Chem. Ber., 88, 1819 (1955).
69. V. D. Pokhodenko, Doctoral Thesis, Institute of Physical Chemistry, Kiev, 1969.
70. V. I. Vedeneev, L. V. Gurvich, and V. N. Kondrat'ev, "Energiya Razryva Khimicheskoi Svyazi. Potentsialy Ionizatsii i Srodstvo k Elektronu" (Chemical Bond Dissociation Energies, Ionisation Potentials, and Electron Affinities), Izd. Akad. Nauk SSSR, 1962.
71. L. Mahoney and M. Da'Rooge, J. Amer. Chem. Soc., 92, 890 (1970).
72. A. L. Buchachenko, M. B. Neiman, O. P. Sukhanova, and Yu. G. Mamedova, Zhur. Fiz. Khim., 37, 221 (1963) [Russ. J. Phys. Chem., No. 1 (1963)].
73. M. Da'Rooge and L. Mahoney, J. Org. Chem., 32, 1 (1967).
74. K. Ley, E. Müller, and W. Schmidhuber, Angew. Chem., 70, 75 (1958).
75. A. L. Buchachenko, E. I. Sdobnov, S. R. Rafikov, and M. B. Neiman, Izv. Akad. Nauk SSSR, Ser. Khim., 1118 (1963).
76. S. G. Kukes, N. N. Bubnov, A. I. Prokof'ev, S. P. Solodovnikov, A. A. Volod'kin, G. A. Nikiforov, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 984 (1972).
77. D. Kh. Rasuleva, A. A. Volod'kin, V. V. Ershov, A. I. Prokof'ev, and S. P. Solodovnikov, Izv. Akad. Nauk SSSR, Ser. Khim., 1659 (1970).
78. A. Streitwieser, "Molecular Orbital Theory for Organic Chemists", New York, 1961, p. 173.
79. A. I. Prokof'ev, S. P. Solodovnikov, A. A. Volod'kin, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 1712 (1968).
80. R. Stebbins and F. Sticilio, Tetrahedron, 291 (1970).
81. G. Hammond, J. Amer. Chem. Soc., 77, 334 (1955).
82. A. I. Prokof'ev, V. M. Chibrikin, V. V. Ershov, and G. A. Zlobina, Collected Papers, Zhur. Strukt. Khim., "Radiospektroskopicheskie i Kvantovokhimicheskie Metody v Strukturnykh Issledovaniyakh" (Microwave Spectroscopic and Quantum-chemical Methods in Structural Investigations), 1967, p. 110.
83. A. A. Volod'kin, V. V. Ershov, A. I. Prokof'ev, S. P. Solodovnikov, and D. Kh. Rasuleva, Izv. Akad. Nauk SSSR, Ser. Khim., 856 (1971).
84. M. Tsubota, J. Chem. Soc. Japan, 89, 608 (1968).
85. V. D. Pokhodenko and N. N. Kalibabchuk, Zhur. Org. Khim., 2, 1397 (1966).
86. A. I. Brodskii, V. D. Pokhodenko, N. N. Kalibabchuk, and V. S. Kuts, Dokl. Akad. Nauk SSSR, 172, 122 (1967).
87. A. I. Prokof'ev, S. P. Solodovnikov, A. A. Volod'kin, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 1104 (1971).
88. A. I. Prokof'ev, S. P. Solodovnikov, A. A. Volod'kin, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 642 (1972).
89. A. I. Prokof'ev, S. P. Solodovnikov, A. A. Volod'kin, Izv. Akad. Nauk SSSR, Ser. Khim., 640 (1972).

90. A. I. Prokof'ev, S. P. Solodovnikov, A. A. Volod'kin, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 933 (1972).
91. A. I. Prokof'ev, S. P. Solodovnikov, A. A. Volod'kin, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 935 (1972).
92. A. I. Prokof'ev, S. P. Solodovnikov, A. A. Volod'kin, and V. V. Ershov, Dokl. Akad. Nauk SSSR, 204, 114 (1972).
93. V. V. Ershov, A. A. Volod'kin, A. L. Buchachenko, D. Kh. Rasuleva, and V. I. Volod'kina, Izv. Akad. Nauk SSSR, Ser. Khim., 972 (1969).
94. V. V. Ershov, D. Kh. Rasuleva, and V. V. Volod'kin, Izv. Akad. Nauk SSSR, Ser. Khim., 956 (1970).
95. A. A. Volod'kin, D. Kh. Rasuleva, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 2801 (1971).
96. N. N. Kalibabchuk, Candidate's Thesis, Institute of Physical Chemistry, Ukrainian SSR Academy of Sciences, Kiev, 1969.
97. A. A. Volod'kin, M. V. Tarkhanova, A. L. Buchachenko, and V. V. Ershov, Izv. Akad. Nauk SSSR, Ser. Khim., 63 (1968).
98. M. Tsubota, J. Chem. Soc. Japan, 89, 602 (1968).
99. E. Müller, K. Ley, and G. Schlechte, Chem. Ber., 90, 2660 (1957).
100. A. A. Volod'kin, V. V. Ershov, V. I. Volod'kina, D. G. Pobedimskii, and D. Kh. Rasuleva, Izv. Akad. Nauk SSSR, Ser. Khim., 2311 (1969).
101. C. Cook, N. Nash, and H. Flanagan, J. Amer. Chem. Soc., 77, 1783 (1955).
102. E. Müller, B. Teissier, and H. Eggensperger, Annalen, 705, 54 (1967).
103. R. Bauer and G. Coppinger, Tetrahedron, 19, 1201 (1963).
104. C. Bohn and T. Campbell, J. Org. Chem., 22, 458 (1957).
105. E. Müller, K. Ley, and G. Schlechte, Angew. Chem., 69, 204 (1957).
106. T. Matsuura and K. Ogura, Yaki Gosei Kagaku Kyokai Shi, 28, 461 (1970).
107. G. Coppinger and T. Campbell, J. Amer. Chem. Soc., 75, 734 (1953).
108. B. Miller, Tetrahedron Letters, 3527 (1964).
109. B. Miller, J. Org. Chem., 30, 1964 (1965).
110. A. V. Volod'kin, M. V. Tarkhanova, V. V. Ershov, and A. L. Buchachenko, Izv. Akad. Nauk SSSR, Ser. Khim., 1583 (1969).
111. V. V. Ershov and A. A. Volod'kin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 893 (1963).
112. M. V. Tarkhanova, Candidate's Thesis, Institute of Organic Chemistry, USSR Academy of Sciences, Moscow, 1971.
113. C. Bamford, G. Eastmond, and D. Whittle, J. Organometal. Chem., 17, 33 (1969).
114. A. A. Volod'kin, V. V. Ershov, and M. V. Tarkhanova, Izv. Akad. Nauk SSSR, Ser. Khim., 1373 (1970).
115. A. A. Blyumenfel'd, L. V. Bryukhovetskaya, G. V. Fomin, and S. M. Shein, Zhur. Fiz. Khim., 44, 931 (1970) [Russ. J. Phys. Chem., No. 4 (1970)].
116. D. G. Pobedimskii, Uspekhi. Khim., 40, 254 (1971) [Russ. Chem. Rev., No. 2 (1971)].
117. M. S. Khloplyankina, A. L. Buchachenko, A. G. Vasil'eva, and M. B. Neiman, Izv. Akad. Nauk SSSR, Ser. Khim., 1296 (1965).
118. A. A. Volod'kin, D. Kh. Rasuleva, V. V. Ershov, A. I. Prokof'ev, S. P. Solodovnikov, N. N. Bubnov, and S. G. Kukes, Izv. Akad. Nauk SSSR, Ser. Khim., 1212 (1972).
119. D. Kh. Rasuleva, A. A. Volod'kin, V. V. Ershov, N. N. Bubnov, A. I. Prokof'ev, S. P. Solodovnikov, and S. G. Kukes, Izv. Akad. Nauk SSSR, Ser. Khim., 1446 (1972).
120. N. N. Bubnov, S. G. Kukes, A. I. Prokof'ev, S. P. Solodovnikov, A. A. Volod'kin, D. Kh. Rasuleva, and V. V. Ershov, Dokl. Akad. Nauk SSSR, 204, 865 (1972).
121. L. Denivelle and M. Hedayatullah, Compt. rend., 253, 2711 (1961).
122. K. Ley and E. Müller, Chem. Ber., 89, 1402 (1956).
123. V. V. Ershov and G. A. Zlobina, Zhur. Org. Khim., 2, 299 (1966).
124. A. Rieker and G. Henes, Tetrahedron Letters, 3775 (1968).

Institute of Chemical Physics,
USSR Academy of Sciences,
Moscow

Institute of Organic
Derivatives of the Elements,
USSR Academy of Sciences,
Moscow