ONE-ELECTRON TRANSFER IN THE DEHYDROAROMATIZATION OF HETEROCYCLIC COMPOUNDS (SURVEY)*

N. T. Berberova and O. Yu. Okhlobystin

UDC 547.543.422

The survey systematizes studies of recent years on the mechanism of the dehydroaromatization of heterocyclic compounds, as well as the dehydrogenation of functionally related systems. The available material is arranged according to types of dehydrogenating agents. On the basis of the literature data and the author's own experimental data, the stepwise mechanism of the oxidative dehydrogenation of heterocyclic compounds is substantiated.

Reactions of dehydroaromatization are an important division of the synthetic chemistry of heterocycles; recently interest in the mechanism of these conversions has increased sharply. This circumstance is clearly associated with the exceptional role that reactions of hydrogenation and dehydrogenation play in biochemistry, where they lie at the basis of cell energetics (NADH → NAD^+, etc.).

Reactions of dehydrogenation, leading to heteroaromatic cations, were originally treated as typical hydride displacement reactions (stripping of a hydride ion). However, in the last 10-12 years the number of indirect data supporting a stepwise character of these reactions has increased rapidly; in the latter case intermediate formation of radical cations of the substrate is postulated. Unfortunately, in virtually none of these scattered cases is the argumentation exhaustive, which creates grounds for incessant debate of the true mechanism of dehydrogenation. In connection with this, the studies in which various independent methods, applied to monotypic objects, lead to convergent results seem the most urgent.

The present survey is not aimed at giving any sort of complete summary of the dehydrogenation reaction and is devoted to a systematization and analysis only of the studies in which the mechanism of these reactions was the subject of experimental study. Preference is given to studies of recent years and reactions of dehydroaromatization; however, it also proved advisable to bring in certain data on the dehydrogenation of functionally related systems.

The purpose of the survey was to outline the general picture that has now developed, while sacrificing a number of details. The available material was arranged according to types of dehydrogenating agents.

Concepts of "hydride" displacements ("transfer" of a hydride ion) were introduced by F. Whitmore in 1932 [1] to explain the isomerization of carbonium ions. Now the question of the nature of the migrant (ion or radical?) in the case of intramolecular rearrangements is scarcely raised at all; according to the prevailing opinion, the actual act of migration occurs in the activated complex, where the migrant does not arise as a kinetically independent particle. The same also pertains to bimolecular reactions, proceeding according to a scheme of cyclic transfer. A. N. and N. A. Nesmeyanov correctly note that in the activated complex displacements of electron pairs and displacements of single electrons are as yet indistinguishable [2]. Thus, the term "transfer" of a hydride ion is inaccurate from the very beginning: In essence, it is not at all a matter of precisely what is being transferred. Recognizing this, D. N. Kursanov and Z. N. Parnes, in their generalizing studies, usually caution against a literal understanding of the term "hydride ion transfer" [3, 4] and emphasize that they have in mind only the gross result of the reaction. Evidently V. I. Minkin, L. P. Olekhnovich, and Yu. A. Zhdanov [5] are correct in calling the isomerization of carbonium ions a reaction of *proton* exchange.

---

*Published to stimulate discussion.

K. L. Khetagurov Severo-Osetinsk State University, Ordzhonikidze 362040. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1011-1025, August, 1984. Original article submitted January 4, 1983.

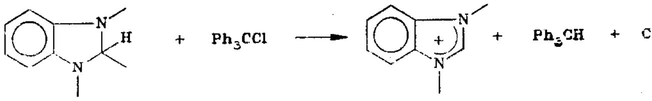
0009-3122/84/2008-0817$08.50

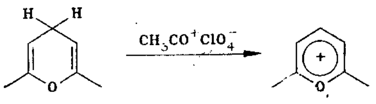
E. Kosower was one of the first to formulate the principle of stepwise transitions from pyridinium salts to dihydropyridines and the reverse; such conversions proceed with intermediate formation of charge transfer complexes (CTC), spectroscopically recorded in a large number of cases [6]. In the case of pyridinium salts with "weak" anions, there is usually even a complete transfer of an electron to the cation with the formation of a radical pair [7].

Organic Cations. The traditional approach to the interpretation of the mechanism of heteroaromatization under the action of organic cations regards bimolecular elimination of a hydride ion as the minimum; there is a summary of such studies in [3].

It is believed that in the limiting step of the reaction, under the action of an electrophilic reagent, there is a one-step stripping of a hydride ion, i.e., a proton together with an electron pair, from a C–H or N–H bond. Stable carbocations [8-11], active carbenium ions [4] ("ionic hydrogenation"), and acylinium cations [7, 8] are used as hydride ion acceptors.

The most characteristic in this respect is dehydrogenation of benzimidazolines under the action of trityl chloride [9, 12, 13], the conversion of cycloheptatriene to a tropylium cation under the action of the tert-butyl cation [14], dehydrogenation of dihydropyridines and nicotinamides by the action of triphenylmethyl chloride, diazonium salts, tropylium fluorobate, etc. [15, 16], and the production of pyrylium salts from pyrans under the action of acetyl perchlorate [17].

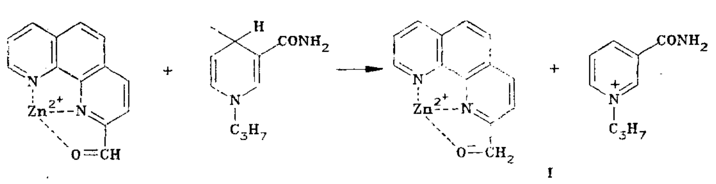




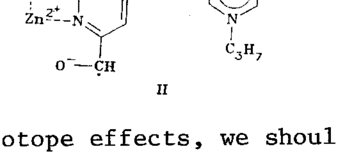
Unfortunately, most of the studies of this group do not contain any significant experimental evidence in support of an ionic mechanism providing for direct stripping of a hydride ion. Exceptions are the analysis of isotope effects and the kinetic data on oxidative dehydrogenation.

On the basis of the fact that in the reaction of N-methyldihydroacridine with substituted o-benzoquinones, the primary isotope effect varies from 4.5 to 13, while the secondary effect is the same for all reactions (1.1), it was concluded [18] that cleavage of the C–H bond occurs in the limiting step, which, in their opinion, is the stripping of a hydride ion.

The noncorrespondence between the kinetic isotope effects of the reduction of 1,10-phenanthroline-2-carbaldehyde by N-propyldihydronicotinamide and triethylammonium borohydride, catalyzed by zinc ions, indicates the formation of a rather stable intermediate, which is recorded spectrophotometrically [19, 20]. The authors believe that the intermediate is the ion pair I but do not exclude the possibility of existence of the radical pair II as well:



I



II

In analysis of the kinetic isotope effects, we should not forget that depending on the experimental conditions and the structure of the substrate, its radical cation may be relatively stable and may break down in the slow step.

Typical examples of the use of kinetic data to substantiate the ionic character of dehydroaromatization are the oxidation of 1,3-dimethylbenzimidazoline by cations dyes [21-23], as well as the homogeneous dehydrogenation by heteroaromatic N-imines [24,25]. In the first case dehydrogenation is described by a second-order equation, in the second by a first-order equation of an irreversible reaction; in both cases the kinetic curves are sigmoid.

A few kinetic data themselves cannot serve as evidence for a synchronous mechanism, since, for example, the total second order observed experimentally may pertain only to the slowest of the consecutive steps. It was found that the oxidation of 1,3-dimethyl-2-phenylbenzimidazoline by the trityl cation and the 2,4,6-triphenylpyrylium cation, since in the studies cited above [21, 22], it is described by a second-order equation, but in this case, even at room temperature, triphenylmethyl and, correspondingly, triphenylpyranyl radicals are recorded by the ESR method [26]. It is characteristic that the pyranyl radical is not formed in the total absence of oxygen; the presence of traces of it is essential for the reaction to occur. Once again R. Hoffman [27] proves correct, since he called for extreme caution in drawing conclusions on the reaction mechanism on the basis of kinetic data without considering the influence of traces of oxygen.

Dehydrogenation under the action of silver cations is cited as convincing evidence in support of a one-step mechanism [28]; however, the hypothesis of intermediate formation of silver hydride proves inadequate, since the liberation of hydrogen, as was found in [27], may occur during the fragmentation of the radical cation of the substrate $RH^{\bullet +} \rightarrow R^{+} + H^{\bullet}$.

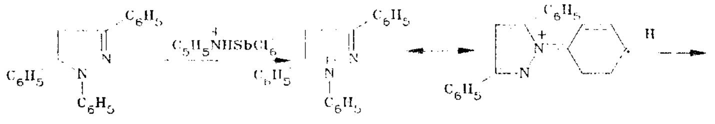
We should also keep in mind that even sodium borohydride may play the role only of an electron donor, not of a hydrogen donor with respect to heteroaromatic cations [29], from which follows the theoretical possibility of a stepwise mechanism in this case also.

The tendency of organic cations for one-electron reduction to free radicals is one of the leading features of their chemical behavior [30]. This pertains to carbenium ions [31], carboxonium [32], diazonium [33, 34], and heteroaromatic cations and many others [35].

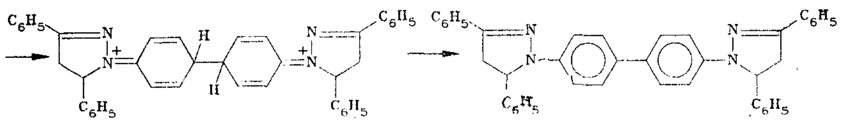
Thus, in each concrete case, the question of the possibility of a stepwise ($-e$, $-H^{+}$, $-e$) mechanism of dehydroaromatization under the action of cations cannot be eliminated without sufficient basis. In a very large number of synthetic studies, reactions of the type of $RH + R'^{+} \rightarrow R^{+} - R'H$ are treated as a one-step hydride transfer, although, as a rule, the mechanism of such reactions has not at all been the subject of experimental investigation. A characteristic situation in this respect is the one that has developed in the preparative chemistry of pyrylium salts [17]. To obtain pyrylium cations from the corresponding pyrans, usually trityl and acetyl perchlorates, which are traditionally considered as "normal" hydride ion acceptors, are used; however, until recently the question of the possibility of a stepwise mechanism was not even raised. Nonetheless, precisely in these and similar models, a stepwise mechanism leading to the formation of radical pairs at the first step has been substantiated.

Ballester et al. [36, 37] used the tris(pentachlorophenyl)methyl cation for the dehydrogenation of cycloheptatriene; instead of the expected tris(pentachlorophenyl)methane, the corresponding stable radical was obtained. This same radical is also formed in the reduction of the cation by 9,10-diphenylanthracene, which is entirely incapable of dehydrogenation. The tris(pentachlorophenyl)methyl cation proved to be a one-electron oxidizing agent with respect to triethylsilane as well; the hydrogenation product is formed as a result of disproportionation of the radical pair that arises [38]. The positive polarization of the methine proton in triphenylmethane, produced from trityl chloride and triethylsilane, also leads to an analogous conclusion [39]. Finally, the existence of a triethylsilane radical cation in solution has been demonstrated by a direct experiment using a rotating disk electrode with a ring [40].

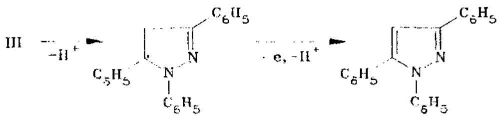
Evidence has been obtained to support the intermediate formation of a radical cation of the substrate in the course of the dehydrogenation of substituted pyrazoline by pyridinium hexachloroantimonate [41]. A product of dimerization of the radical cation is formed in acetonitrile and chloroform:



III



In proton acceptor medium (in pyridine) the reaction occurs differently — the initially formed pyrazoline radical cation is rapidly deprotonated, and oxidation of the neutral pyrazolinyl radical leads to 1,3,5-triphenylpyrazole:



Evidently, the reverse reaction — the addition of hydrogen to organic cations — also proceeds in stages (+e, +H$^+$, +e or +e, +H). We have found no literature data that would seriously contradict this assertion.

Ionic Hydrogenation. D. N. Kursanov, Z. N. Parnes, and their associates have discovered a reaction of "ionic" hydrogenation, the mechanism of which was for a long time understood as successive addition of a proton (forming a carbocation) and a hydride ion to a multiple bond, the hydride ion being donated by triethylsilane [3, 4, 42, 43]. In addition to silanes, other hydrogen sources are also used in reactions of this type — 9,10-dihydroanthracene [46], cycloheptatriene [47], etc. We should mention the sharp increase in the reaction rate in the presence of catalytic amounts of lithium perchlorate (less than 1%), which finds no satisfactory explanation within the framework of the original reaction scheme [45]. Only quite recently have the authors arrived at the conclusion of a stepwise mechanism of the final step, which formally corresponds to hydride ion transfer [44].

The possibility of "ionic" hydrogenation using gaseous hydrogen in the presence of phosphine complexes of platinum or palladium as transmitters of hydride hydrogen has been discovered [48, 49]. In the dehydrogenation of 1,4-dihydropyridines in trifluoroacetic acid in the presence of the phosphine complex of Pd(0), liberation of hydrogen capable of quantitatively and selectively hydrogenating 1,5-cyclooctadiene has been observed [50].

The impression is created that despite the abundance of factual data on ionic hydrogenation and the intensive development of this interesting approach, the mechanism of the final step of the gross process has not yet been sufficiently studied; however, a stepwise mechanism, beginning with one-electron oxidation of a donor of "hydride" hydrogen seems more probable.

Lewis Acids and Peracids. Many dehydrogenation reactions practically do not occur in the absence of Lewis acids [51, 52]. Most of the authors who have studied dehydrogenation under the action of Lewis acids [53, 54] are inclined to consider the formation of ion pairs of the type $R^+AlCl_4^-$, where R^+ is a carbenium or carboxynium ion, to which the role of hydride ion acceptor is attributed . We should not forget in this case that the carbocation can also play the role of a one-electron oxidizing agent.

Lewis acids — $AlCl_3$, BF_3 — in a medium of organic solvents are frequently used in the role of powerful one-electron oxidizing agents [55, 56]. The concrete mechanism of such action remains unclear — it would be difficult to agree that, let us say, Al^{3+} might be readily reduced to Al^{2+} in one step, etc. The interesting opinion has been expressed that the oxidative properties of the aluminum chloride—nitromethane system are related to the appearance of an unsolvated proton [57]; in other words, such systems play the role of peracids, which possess a high protonating capacity.

In certain cases, dehydrogenation is accompanied by the liberation of free hydrogen; it is believed [58] that this is clear evidence of an ionic mechanism. We are speaking, in particular, of the formation of a carbocation under the action of an Ol acid ($HOSO_2F + SbF_5$) on isobutane [59]. It is clear, however, that R^+ cations may be formed according to the scheme $RH \overset{-e}{\rightleftarrows} RH^{\cdot +} \rightarrow R^+ + H^\bullet$ (breakdown to $R^\bullet$ and H^+ is hindered in strongly acid medium) or according to the same Ol scheme of addition-elimination described, for example $CH_4 \overset{+H^+}{\rightleftarrows} CH_5^+ \rightarrow CH_3^+ + H_2$.

It is almost obvious that dehydrogenation under the action of Lewis acids and peracids is essentially a particular case of dehydrogenation under the action of carbocations or radical ions (see below).

"Two-Electron" Oxidizing Agents. L. Michaelis (see below) advanced the postulate that the elementary steps of organic redox reactions are always one-electron steps. Earlier, in speaking about electrochemical reactions, N. N. Semenov [60] noted that "... in one step one electron is transferred, since the simultaneous transfer of two electrons is a significantly less probable event." Nonetheless, E. Kosover [61] considers it necessary to distinguish the action of two-electron oxidizing agents, stipulating the impossibility of genuinely two-electron transfer without the participation of a "bridge" atom or a "bridge" group [62]. As an example of two simultaneously occurring one-electron transitions, leading to the formation of a covalent bond, we might cite the halogenation of enolizing compounds by copper halides [63] and the oxidation of ascorbic acid by Cu^{2+} salts [64].

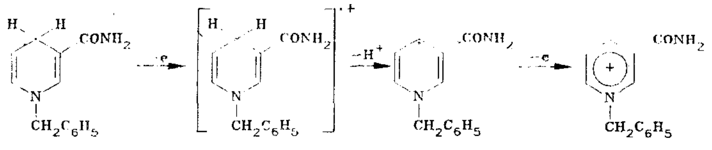
From the standpoint of kinetics, the concept of simultaneity means only that the transfer of a second electron occurs more rapidly than that of the first, but precisely from this it follows that the limiting step of the gross process is the transfer of the one first electron. The transfer of two, three, etc., electrons always occurs in stages [61], with the exception of cases when the summary process represents an aggregate of several synchronous one-electron processes (for example, in template synthesis), proceeding mutually independently. In a characteristic case, the electrochemical reduction of symmetrical bis-pyrylium cations proceeds in one two-electron wave if the cationic sites are separated by a nonconducting chain [65]; it is clear that each of them is reduced independently of the other. The relative nature of the concept of simultaneity is indicated by W. Basolo and I. Pearson in their book [66].

Neutral Molecules. The most typical and well studied process of dehydrogenation under the action of neutral molecules is the dehydrogenation by quinones, which is close to natural biochemical reactions. It was precisely on the example of these reactions that L. Michaelis formulated the general principle of organic redox reactions in 1939: In each elementary step only one electron is transferred [67]. This idea, accepted at first by most researchers as a postulate, was confirmed in subsequent years by numerous experimental data. Investigations of the elementary steps of a wide circle of organic reactions led to the discovery of facts that could be explained only from the standpoint of one-electron transfer [68, 69].

Quinones are considered as splendid dehydrogenating agents in the production of stable aromatic and heteroaromatic cations. The general scheme of such reactions on the example of the interaction of perinaphthene with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in neutral and acid media was proposed in [70]: $RH_2 + E \rightarrow RH + EH$; $RH^{\bullet} + EH^{\bullet} \rightarrow RH^{+} + EH^{-}$. If the free radical formed is sufficiently stable, then instead of the formation of a cation there is a further accumulation of a free radical $RH_2 + EH^{\bullet} \rightarrow RH^{\bullet} + EH_2$. Since the rate of hydrogenation of quinones is a linear function of their reducing potentials [71], the proposed scheme seems quite plausible.

In the course of the hydrogenation of thiobenzophenone by 1-benzyl-1,4-dihydronicotinamide, signals of the thiobenzoquinone radical anion and the dihydronicotinamide radical cation, the distance between which is estimated at 6 Å, are observed in the ESR spectra at low temperatures [72]. When the temperature is raised, only the thiyl radical is observed. Conclusion: At the first step a charge transfer complex is formed; the second step, which determines the reaction rate, is the transfer of a proton from the dihydronicotinamide radical cation to the thiobenzoquinone radical anion; the third step is spontaneous transfer of a second electron, leading to the reaction products [73].

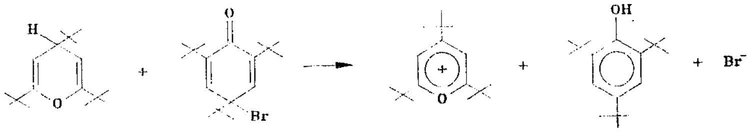
In the dehydrogenation of 1,4-dihydronicotinamide by gem-bromonitropropane, the ESR spectrum of nitropropane is recorded; nitropropane and the corresponding pyridinium bromide were preparatively isolated [74]:



$$(CH_3)_2C(NO_2)Br \xrightarrow{+e} \cdots\cdots \xrightarrow[Br]{} (CH_3)_2\dot{C}NO_2 \longrightarrow (CH_3)_2CHNO_2$$

Kinetic measurements (first order with respect to each of the reagents; $k = 3.172 \cdot 10^{-3}$ liter/mole•sec) also agree with the scheme cited.

The conversion of pyrans to pyrylium salts under the action of typical one-electron reducing agents has been studied. Thus [75], 2,4,6-tri-tert-butyl-4H-pyran is converted to tri-tert-butylpyrylium under the action of "quinobromide," 4-bromo-2,4,6-tri-tert-butylcyclohexadienone:



Since the most characteristic reaction of quinobromide is the capture of one electron with the formation of a stable phenoxyl radical [76], there is sufficient basis for believing that the first step of the reaction is precisely one-electron transfer. Tetracyanoquinodimethane (TCNQ) behaves toward pyrans analogously to the quinobromide: Even at room temperature a well resolved ESR spectrum of the $TCNQ^{\bullet-}$ radical anion is readily recorded [77].

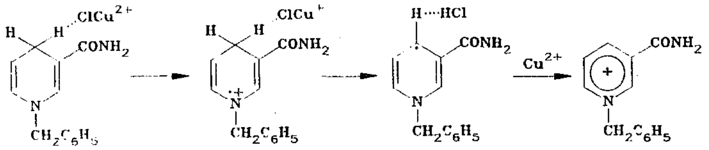
In a number of related cases the formation of charge transfer complexes was recorded spectrophotometrically [19, 20, 78].

It should be mentioned that in certain studies one-step stripping of a hydride ion is postulated only on the basis of the absence of ESR signals [25, 79] or dynamic polarization of nuclei [80]. Such attempts are incorrect in principle: The absence of an ESR signal means only that the radical concentration does not exceed 10^{12} spins/ml under the experimental conditions; consequently, the conclusion of total absence of triplet intermediates is clearly premature. The DPN method is informative in general only in the presence of a nuclear polarization effect [81].

Ions of Variable Valence. The dehydrogenation of many biologically important substrates proceeds with the participation of ions of variable valence, contained in coenzymes [6, 82]. In a number of studies reactions of this type have been investigated at the stoichiometric and kinetic levels.

The oxidation of $Fe^{2+} \rightarrow Fe^{3+}$ by diphenylpicrylhydrazyl in aqueous alcohol medium is accompanied by transfer of hydrogen from the alcohol [83]; however, it is unclear whether there is first a transfer of an electron to diphenylpicrylhydrazyl, followed by protonation, or whether the reaction proceeds as a transfer of a hydrogen atom from the solvent contained in the coordination sphere of Fe^{2+} [84].

The dehydrogenation of dihydronicotinamide by Cu^{2+} salts does not occur under the action of copper sulfate, acetate, and nitrate, but is observed only in the case of the bromides and chlorides [85]. Probably the halide ion is a bridge that links the dihydronicotinamide molecule to the copper ion; moreover, the halide ion stabilizes the monovalent copper ion formed:



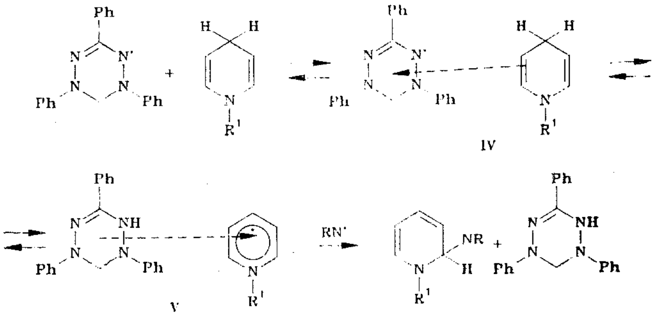
The dehydrogenation of acridans by divalent copper salts has been described [86].

Reactions of autooxidation in the presence of ions of variable valence — Co, etc. — are close to the group of reactions under consideration (see below).

Free Radicals and Radical Ions. The ability of free radicals to strip off hydrogen atoms is a generally recognized property of them; thus, there is no question of their ability for heteroaromatization of various substrates; however, there have been few studies devoted to the mechanism of such reactions. In connection with this, it seems necessary to consider some studies of the mechanism of related reactions of dehydrogenation of amines by stable nitroxyls.

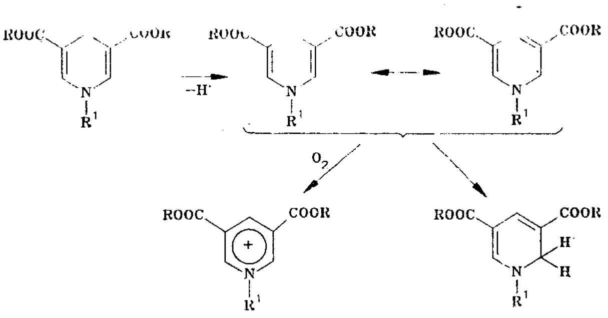
É. G. Rozantsev et al. [87], studying the kinetics of the dehydrogenation of hydrazobenzene by stable nitroxyls, arrived at the conclusion that there are two successive steps of stripping of hydrogen atoms. This conclusion is by no means indisputable, since the ability of free radicals for stepwise capture of a hydrogen atom (+e, $+H^+$) has become known [88, 89]. The rate of dehydrogenation of N,N'-disubstituted p-phenylenediamines by various nitrogenous radicals increases with increasing acidity of the medium [90]. Consequently, the real dehydrogenating agent in this case is a protonated form of the radical, i.e., a radical cation: $R^{\bullet} + H^+ \rightleftarrows RH^{\bullet +}$; $RH^{\bullet +} + AH_2 \rightarrow RH + AH_2^{\bullet +}$, etc., where $R^{\bullet}$ is a stable radical, and AH_2 is a dehydrogenating substrate. The experimental reaction kinetics corresponds to this scheme. In the opinion of A. L. Buchachenko and A. M. Vasserman [91], this result means that in neutral medium there is a transfer of a hydrogen atom in the absence of catalysis, whereas under conditions of a catalytic reaction in acid medium the limiting step is electron transfer. Let us recall once again that in principle the transfer of a hydrogen atom can occur in steps (−e, $-H^+$).

The dehydrogenation of dihydropyridines, by triphenylverdazyl radicals [92-94] is described by a second-order kinetic equation with first order with respect to each reagent [95]:



At the first step a charge transfer complex (IV) is formed between dihydropyridine and the solvated radical $RN^{\bullet}$; the limiting step is transfer of hydrogen to triphenylverdazyl, forming a different complex (V), which reacts rapidly with the second radical. It is believed, however, [96] that dehydrogenation under the action of the triphenylverdazyl cation proceeds as transfer of a hydride ion, despite the evident possibility of intermediate formation of a verdazyl radical.

The method of UV spectroscopy has been used to study the free-radical dehydrogenation of dihydropyridines by the agency of diphenyl picrylhydrazyl in acetonitrile [97]. The authors believe that diphenylpicrylhydrazyl splits off hydrogen in the limiting step. The pyridyl radicals formed, interacting with atmospheric oxygen or with diphenylpicrylhydrazyl, are converted to pyridinium cations; in the absence of oxygen the dehydrogenation of dihydropyridines does not occur at all, and only a rearrangement to 1,2-dihydropyridines is observed.



An inhibition of free radical reactions by 1,4-dihydropyridines is detected, which is evidence of an easy removal of hydrogen by 1,4-dihydropyridines [98].

It is clear that the dehydrogenation of hydroaromatic systems under the action of free radicals cannot be interpreted as a one-step transfer of a hydrogen ion, no matter how much we might wish it.

Oxygen. Evidently free oxygen can play the role of a dehydroaromatizing agent and in general a dehydrogenating agent in a number of cases; however, in this case the participation of a third reagent (catalyst) is usually necessary. We might indicate, for example, the autooxidation of 9,10-dihydroanthracene in the presence of free nitroxyl [99]; the reaction becomes catalytic as a result of oxidation of the hydroxylamine formed by atmospheric oxygen. In a series of studies by M. E. Vol'pin et al. [100-102], complexes of transition metals were used as catalysts of the autooxidation of NADH. A mechanism has been proposed for catalytic autooxidation, including intermediate formation of a complex of the catalyst with NADH and oxygen:

$$[\mathrm{Co}]+\mathrm{NADH\ H}+\mathrm{O_2}\rightleftharpoons[\mathrm{Co}]\cdot\mathrm{NADH}\cdot\mathrm{H}\cdot\mathrm{O_2};$$
$$[\mathrm{Co}]\cdot\mathrm{NADH}\cdot\mathrm{H}\cdot\mathrm{O_2}\rightarrow[\mathrm{Co}]+\mathrm{NADH^+}+\mathrm{HO_2^{\cdot}}.$$

In this case the complex of Co^{2+} is gradually oxidized to Co^{3+}. The catalytic activity of a number of Fe^{3+} metalloporphyrins, in which there are no tightly bound axial ligands, has also been studied [101].

K. B. Yatsimirskii et al. [103] have suggested a mechanism of autooxidation of ascorbic acid, including the elimination of hydrogen ions from the substrate by an oxygenated complex of Co^{2+}.

We should keep in mind that autooxidation in the presence of ions of variable valence is usually of a free-radical chain type [82, 104, 105]. The first step of the reduction of oxygen is a one-electron transfer with the formation of a superoxide radical anion [82, 105]; it can scarcely be doubted that electron transfer is an essential step of reactions in which free oxygen participates.

The dehydrogenation of dihydroquinolines [106] and 4H-pyrans by carbon tetrachloride [107] also proceeds according to a free-radical mechanism; in the latter case an ionic mechanism has been substantiated [107].

In a number of cases the dehydrogenation by oxygen also proceeds without the participation of a catalyst. Thus, diperimidine is readily dehydrogenated in air with the formation of tetraazapyrene [108, 109]:

The autooxidation of 2,4,6-triphenyl-4H-pyran [76] is substantially facilitated in the presence of electrolytes. Evidently the presence of an electrolyte facilitates the separation of charges in the complex of the substrate with oxygen initially formed. The reaction rate depends substantially on the nature of the cation of the electrolyte [40]. The difference in the action of cations is evidently determined by the different stability of the corresponding superoxides. A catalytic action of magnesium, zinc, and lithium perchlorates on the one-electron oxidation of dihydropyridines by fluorinated ketones has been detected [110, 111]. The authors explain the different accelerating effects of cations by complex formation of the cations with the substrate.

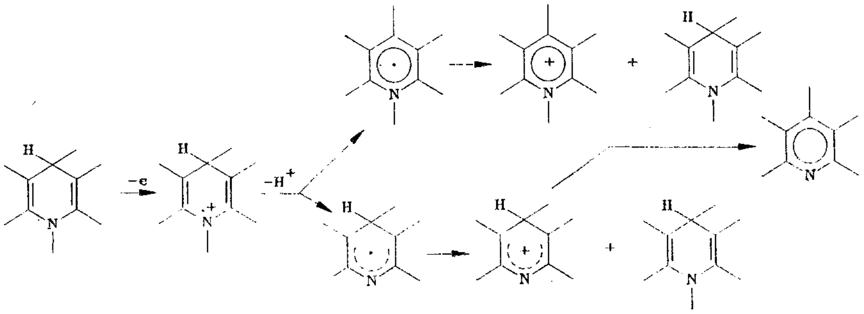
It is clear that oxygen can play an important and multifaceted role in reactions of dehydrogenation; in particular, it itself can act as a catalyst and electron transporter.

Electrochemical Dehydrogenation. The greatest successes in the understanding of the mechanism of reactions of dehydrogenation have been achieved thanks to the use of the electrochemical modeling of organic reactions. This has been promoted especially by work in aprotic media, since in this case the multielectron steps that are common for aqueous media can be separated into simple elementary steps of electron transfer, and the intermediate products can be registered.

From the beginning electrochemists have treated the mechanism of dehydrogenation reactions as a stepwise process. Unfortunately, on account of the absence of the proper contact between organic chemists and electrochemists, each group has remained ignorant of the activities of the other. Indicative in this sense is the study of the mechanism of the dehydrogenation of cycloheptatriene. Organic chemists have traditionally treated this reaction as a one-step transfer of a hydride ion [112-114]. The work of D. Geske [115] (1959), who studied the oxidation of cycloheptatriene in acetonitrile chromopotentiometrically, remained unnoticed. On the chronopotentiometric curve with current reversal, oxidation of tropylidene, reduction of a proton, and reduction of a tropylium cation were recorded. Thus, not the hypothetic hydride ion but a quite real proton was recorded as the kinetically independent particle.

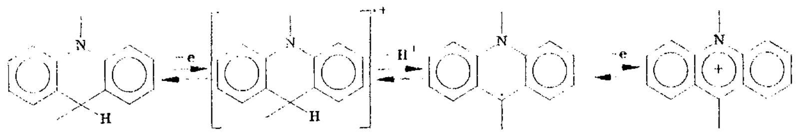
The rate of oxidation of dihydropyridines by quinones is directly related to the redox potentials [71], which can be considered as important evidence in support of a stepwise mechanism of dehydrogenation, beginning with one-electron transfer.

The development of concepts of a stepwise mechanism of the dehydroaromatization of heterocyclic compounds was promoted to a substantial degree by the successes of the chemistry of heterocyclic radical cations and the recognition of the important role of the latter in a wide circle of reactions of heterocycles [116]. It has been suggested [117] that in readily oxidized dihydropyridines, there is a hydride displacement, whereas in difficultly oxidized substrates a one-electron oxidation is possible in the first step. Further studies of these authors have shown that regardless of the value of the oxidation potential, dihydropyridines split out the "hydride ion" in stages [118, 119]. Thus, in the oxidation of 2,6-dimethyl-3,5-diethoxycarbonyl-1,4-dihydropyridines in acetonitrile on a rotating disk electrode with a ring, a one-electron wave is registered on the disk at 0.5-0.8 V, while on the ring two waves are reported, the first of which corresponds to reduction of a proton, and the second to reduction of the corresponding pyridinium cations [118]. The coulometric determination of the number of electrons also clearly indicates a one-electron character of the process. The end product — the pyridinium cation — corresponds to the loss of two electrons; the authors explain this fact by disproportionation of the intermediate free radical:



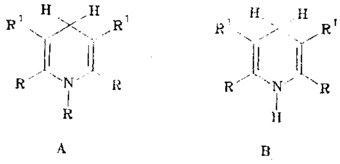
In a study of the oxidation of dihydropyridines on platinum and graphite electrodes in buffered solutions of acetonitrile, a dependence of $+E_{1/2}$ on the pH of the medium was detected in the range of pH from 2 to 8, which is evidence of a potential-determining influence of stripping of a proton on the step of deprotonation of the radical cations [119].

In the oxidation of acridans, I. M. Sosnkin et al. [86], using the "disk-ring" method, recorded the formation of radical cations of the substrate; recording of the volt—ampere curves at a constant potential of the disk showed that in addition to the main wave of oxidation, a cathodic-anodic wave is observed, corresponding to the conversion of the acridine radical to an acridinium salt:



The proposed scheme was confirmed by a chemical experiment: Oxidation of the dihydrocompound by Cu^{2+} cations leads to the corresponding cation; Cu^{2+} is converted to Cu^+, and two equivalents of Cu^{2+} are consumed per mole of acridan. Recently all the intermediate products arising in the course of the reaction were identified: the acridan radical cation, the proton (cyclic voltamperometry), and the acridinyl radical [120, 121]. It is also asserted that another sequence of elementary steps is possible: $-e$, $-e$, $-H^+$ for dihydrodicyano derivatives of azines and $-H^+$, $-e$, $-e$ for 9-cyano-10-methyl-9,10-dihydroacridan [122].

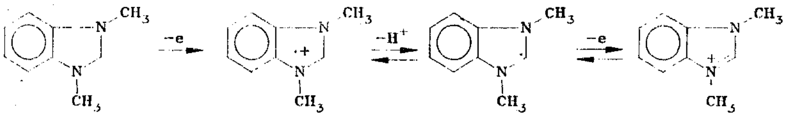
The method of cyclic voltamperometry on a stationary platinum electrode and the method of coulometry have been used to study the mechanism of the anodic oxidation of a number of dihydropyridines [123]:



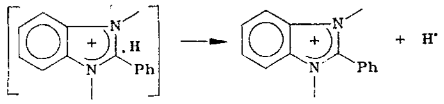
$R = CH_3, R' = COOEt$

Oxidation in acetonitrile proceeds only by half ($E_{1/2}$ = 0.816 V), since the protons arising in the oxidation of the depolarizer form a salt with it, which is not oxidized at the given potential. In the presence of a base (γ-picoline), oxidation occurs with the consumption of two electrons, i.e., goes to completion. On the cyclic voltamperogram of dihydropyridine there is a cathodic peak corresponding to the reduction of the protonated amide to molecular hydrogen. This result agrees with the conclusion of the potential-determining influence of stripping of a proton [124].

Unfortunately, the schemes of dehydrogenation cited are not always so convincingly supported. Thus, in the oxidation of 1,3-dimethylbenzimidazoline in acetonitrile by the method of cyclic voltamperometry, S. Nelson et al. [125] observed an entirely reversible two-electron peak (+0.31 V). The corresponding cation is reduced only at 2 V. On the basis of these data alone the authors suggested the following mechanism of dehydrogenation:



Not one of the intermediate products was registered by the authors, i.e., there is essentially no evidence for the proposed scheme. It was found that actually the benzimidazoline radical cation breaks down, liberating a hydrogen atom [26]:



Despite the well-known tendency of atomic hydrogen for various "adhesion" reactions, an appreciable part of it is liberated in the form of molecular hydrogen by oxidation by silver perchlorate in acetonitrile. When 1,3-dimethyl-2-phenylbenzimidazoline is irradiated in a matrix of aqueous sulfuric acid (77°K), atomic hydrogen can be observed directly by the ESR method (doublet with splitting 500 Oe).

Sometimes initially convincing evidence against a redox mechanism of dehydrogenation is cited [126]. Thus, the measured rate constants of the extinguishment of the fluorescence of 1-benzyl-1,4-dihydronicotinamide by various electron acceptors are several orders of magnitude higher than those calculated theoretically for one-electron oxidation of the substrate. This might seem to exclude the possibility of electron transfer in the limiting steps; however, the authors themselves note that in the presence of a catalyst the barrier to transfer may be substantially lower. Actually, situations are possible in which the reaction does not go at all in the absence of a catalyst — neither according to a synchronous mechanism nor according to a stepwise mechanism. It is very important that oxygen, traces of which are contained in the reaction medium saturated with argon, may act as such a catalyst. It has been shown on the example of the dehydrogenation of 2,4,6-triphenyl-4H-pyran [76] that in this case a stepwise mechanism is realized:

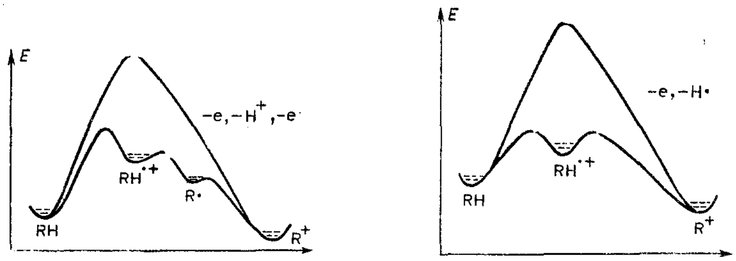
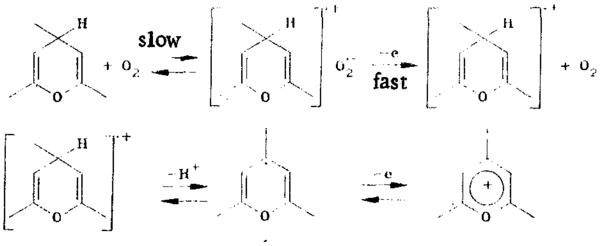


Fig. 1. Energy profiles of dehydrogenation reactions.



It would be a methodological error to draw exhausitve conclusions on the basis of electrochemical model study alone [127-131]. More reliable are the conclusions drawn from the data of several independent methods; in particular, any reaction scheme should not contradict the kinetic data. Considering all these circumstances, the dehydrogenation of 4H-pyrans, 1,3-dimethyl-2-phenylbenzimidazoline, and a number of perimidines has been investigated [130].

An analysis of the available data leads to the assertion that the formal transfer of a hydride ion actually occurs in stages and begins with one-electron oxidation of the substrate, leading to a radical cation. The electrochemical data can be used to predict the type of decomposition of the intermediate radical cations formed [130]. If the substrate is oxidized at low values of $+E_{1/2}$ (in these cases $-E_{1/2}$ of the corresponding cations are relatively high), dehydrogenation proceeds according to a $-e$, $-H^{\bullet}$ scheme; high values of $E_{1/2}$ for the substrate and low $-E_{1/2}$ for the cations predetermine a $-e$, $-H^{+}$, $-e$ mechanism. It is evident that the proton acceptor properties of the medium also affect the direction of the decomposition.

The question of the theoretical possibility of stepwise stripping of a hydride ion, leading to a heteroaromatic cation, is in need of further discussion. The following considerations should be taken into account. Dehydrogenation in essence is a redox reaction. The direct stripping of a hydride ion is possible in the case when a one-electron transfer from the substrate to the dehydrogenating agent is hindered for some reason; in other words, the substrate should not be a reducing agent with respect to the reagent. Such a situation seems rather improbable, since one-electron oxidation of the substrate proceeds through a lower activation barrier: An electron is more readily stripped from the substrate than a hydride ion [13].

The two types of dehydrogenation discussed above can be represented in the form of cross-sections of the potential energy surface (Fig. 1); the envelope curve corresponds to synchronous stripping of a hydride ion. In various kinds of calculations, comparisons of redox potentials, and a study of the kinetics of dehydrogenation reactions, we must constantly keep in mind the possibility (and sometimes even the necessity) of catalysis, in particular, catalysis by oxygen.

LITERATURE CITED

1. F. C. Whitmore, J. Am. Chem. Soc., 54, 3274 (1932).
2. A. N. Nesmeyanov and N. A. Nesmeyanov, Principles of Organic Chemistry [in Russian], Khimiya, Moscow (1970), Book 2, p. 600.
3. Z. N. Parnes and D. N. Kursanov, The Reaction of Hydride Displacement in Organic Chemistry [in Russian], Nauka, Moscow (1969), p. 94.
4. M. I. Kalinkin, G. D. Kolomnikova, and Z. N. Parnes, Usp. Khim., 48, 613 (1979).
5. V. I. Minkin, L. P. Olekhnovich, and Yu. A. Zhdanov, Molecular Design of Tautomeric Systems [in Russian], Izd. Rostovsk. Gos. Univ., (1977), p. 34.
6. E. Kosover, Molecular Biochemistry, McGraw-Hill (1962).

7. V. B. Panov, M. V. Nekhoroshev, and O. Yu. Okhlobystin, Zh. Org. Khim., 49, 234 (1979).
8. V. G. Kharchenko, A. F. Blinokhvatov, K. V. Mityurina, Z. N. Parnes, and D. N. Kursanov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 612 (1974).
9. A. V. El'tsov and Kh. A. Muravich-Aleksandr, Zh. Org. Khim., 1, 1673 (1965).
10. W. Bontrone and D. H. Reid, J. Chem. Soc., Sept-Oct., 2773 (1959).
11. W. Bontrone and D. H. Reid, Chem. Ind., No. 38, 1192 (1960).
12. A. V. El'tsov and M. Z. Girshovich, Zh. Org. Khim., 3, 1332 (1967).
13. A. V. El'tsov, Zh. Org. Khim., 3, 199 (1967).
14. D. Bryce-Smith and N. A. Perkins, Chem. Ind., No. 20, 1022 (1959).
15. N. T. Ioffe, L. Yu. Yuzefovich, and V. G. Mairanovskii, Teor. Eksp. Khim., 14, 389 (1979).
16. O. M. Grishin and A. A. Yasnikov, Ukr. Khim. Zh., 34, 70 (1968).
17. G. N. Dorofeenko, E. I. Sadekova, and E. V. Kuznetsov, Preparative Chemistry of Pyrylium Salts [in Russian], Izd. Rostovsk. Gos. Univ. (1972), p. 227.
18. A. K. Colter, G. Saito, and F. J. Sharom, Can. J. Chem., 55, 2741 (1977).
19. D. J. Creighton, J. Hajdu, and D. S. Sigman, J. Am. Chem. Soc., 95, 6855 (1973).
20. D. J. Creighton, J. Hajdu, and D. S. Sigman, J. Am. Chem. Soc., 98, 4619 (1976).
21. A. V. El'tsov, N. V. Pavlish, and V. A. Ketlinskii, Zh. Org. Khim., 14, 1751 (1978).
22. V. A. Ketlinskii, A. V. El'tsov, and N. V. Pavlish, Zh. Org. Khim., 11, 2219 (1975).
23. C. A. Bunton, S. K. Huang, and C. H. Paok, Tetrahedron Lett., No. 18, 1445 (1976).
24. S. V. Zalyalieva, Author's Abstract of Dissertation for the Degree of Candidate of Chemical Sciences, Moscow (1980).
25. S. V. Zalyalieva, Yu. V. Kurbatov, O. S. Otroshchenko, A. S. Sadykov, and R. Azzamova, Khim. Geterotsikl. Soedin., No. 6, 813 (1973).
26. N. T. Berberova, E. P. Ivakhnenko, A. S. Morkovnik, and O. Yu. Okhlobystin, Khim. Geterotsikl. Soedin., No. 12, 1696 (1979).
27. R. W. Hoffmann, Mechanisms of Chemical Reactions [Russian translation], Khimiya, Moscow (1979), p. 19.
28. V. A. Blinokhvatov, Z. N. Parnes, V. G. Kharchenko, and D. N. Kursanov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 8, 1831 (1974).
29. A. S. Morkovnik, O. Yu. Okhlobystin, and N. M. Dobaeva, Khim. Geterotsikl. Soedin., No. 10, 1428 (1979).
30. L. A. Polyakova, Dissertation for the Degree of Candidate of Chemical Sciences [in Russian], Moscow State University (1973).
31. K. A. Bilevich, N. N. Bubnov, and O. Yu. Okhlobystin, Priroda, No. 5, 4 (1971).
32. V. B. Panov, M. V. Nekhoroshev, and O. Yu. Okhlobystin, Dokl. Akad. Nauk SSSR, 243, 372 (1978).
33. K. A. Bilevich, N. N. Bubnov, B. Ya. Medvedev, L. V. Ermanson, and O. Yu. Okhlobystin, Dokl. Akad. Nauk SSSR, 193, 383 (1970).
34. B. Ya. Medvedev, L. A. Polyakova, K. A. Bilevich, N. N. Bubnov, and O. Yu. Okhlobystin, Teor. Eksp. Khim., No. 8, 256 (1972).
35. K. Wallenfels and M. Gellvich, Ann. Chem., No. 621, 149 (1959).
36. M. Ballester, J. Riera-Fugueras, J. Castaver, and A. Rodriguez-Surana, Tetrahedron Lett., No. 23, 2079 (1971).
37. M. Ballester, J. Riera, J. Castaver, D. Badia, and J. Monso, J. Am. Chem. Soc., 93, 2215 (1971).
38. Z. N. Parnes, Yu. I. Lyakhovetskii, N. N. Bubnov, N. M. Vilkova, S. A. Gabrielyan, and D. N. Kursanov, in: Mechanisms of Heterolytic Reactions [in Russian], Nauka, Moscow (1976), p. 172.
39. I. P. Beletskaya, S. V. Rykov, V. B. Volkova, A. L. Buchachenko, and A. V. Kessenikh, Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 684 (1972).
40. N. T. Berberova, Dissertation for the Degree of Candidate of Chemical Sciences, Gor'kii (1980).
41. A. S. Morkovnik and O. Yu. Okhlobystin, Zh. Geterotsikl. Soedin., No. 1, 128 (1979).
42. D. N. Kursanov and Z. N. Parnes, in: 11th Mendeleev Conference on General and Applied Chemistry [in Russian], Nauka, Moscow (1974), p. 7.
43. D. N. Kursanov, Z. N. Parnes, T. A. Bassova, N. M. Loim, and B. U. Zhdanovich, Tetrahedron, 27, 2235 (1967).
44. Yu. I. Lyakhovetskii, Dissertation for the Degree of Candidate of Chemical Sciences, Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow (1982).
45. Z. N. Parnes, G. D. Kolomnikova, M. I. Kalinkin, and D. N. Kursanov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 8, 1911 (1975).

46. D. N. Kursanov, Z. N. Parnes, and G. I. Bolestova, Izv. Akad. Nauk SSSR, Ser. Khim., No. 5, 1155 (1968).
47. G. D. Kolomnikova and Z. N. Parnes, Usp. Khim., 36, 1721 (1967).
48. D. N. Kursanov, Z. N. Parnes, N. M. Loim, and G. V. Bakalova, Dokl. Akad. Nauk SSSR, 179, 1106 (1968).
49. Z. N. Parnes, G. A. Khotimskaya, M. Yu. Lukina, and D. N. Kursanov, Dokl. Akad. Nauk SSSR, 178, 620 (1968).
50. U. M. Dzhemilev, A. Z. Yakunova, S. K. Minsker, and G. A. Tolstikov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 678 (1968).
51. C. D. Nenitzesku, Usp. Khim., 26, 299 (1957).
52. G. Baddeley, H. T. Taylor, and W. Pickles, J. Chem. Soc., No. 1, 124 (1953).
53. C. D. Nenitzescu, M. Avram, and E. Sliam, Bull. Soc. Chim. Fr., No. 10, 1266 (1955).
54. G. Baddeley and R. Williamson, J. Chem. Soc., No. 7, 2120 (1953).
55. V. D. Pokhodenko, V. A. Khizhnyi, V. G. Koshechko, and O. I. Shkrebtii, Zh. Org. Khim., 11, 1873 (1975).
56. Ya. M. Paushkin and L. M. Osipova, Dokl. Akad. Nauk SSSR, 103, 439 (1955).
57. D. Baner and A. Foucalt, Compt. Rend., 272, 192 (1971).
58. I. P. Beletskaya and A. N. Kashin, Zh. Vses. Khim. Ova., 24, 155 (1979).
59. H. Hogoveen and A. F. Bickel, Chem. Commun., No. 13, 635 (1967).
60. N. N. Semenov, Some Problems of Chemical Kinetics and Reactivity [in Russian], Izv. Akad. Nauk SSSR (1958), p. 257.
61. E. M. Kosover and S. W. Baner, J. Am. Chem. Soc., 82, 2191 (1960).
62. D. L. Leussing and L. Nuwman, J. Am. Chem. Soc., 78, 552 (1956).
63. E. M. Kosover, W. J. Cole, G. Meisters, and G. S. Wu, J. Am. Chem. Soc., 82, 2191 (1960).
64. R. F. Jamerson and N. Blackbroun, J. Chem. Soc., No. 16, 1956 (1976).
65. N. T. Berberova, G. N. Dorofeenko, and O. Yu. Okhlobystin, Khim. Geterotsikl. Soedin., No. 3, 318 (1977).
66. F. Basolo and R. G. Pearson, Mechanisms of Inorganic Reactions, Wiley (1967).
67. L. Michaelis, Biol. Chem., No. 5, 703 (1939).
68. K. A. Bilevich and O. Yu. Okhlobystin, Usp. Khim., 37, 2163 (1968).
69. O. Yu. Okhlobystin, Electron Transfer in Organic Reactions [in Russian], Izv. Rostovsk. Gos. Univ. (1974), p. 121.
70. H. A. S. Reid, M. Fraser, B. B. Molloy, M. A. S. Paune, and R. G. Satorland, Tetrahedron Lett., No. 15, 530 (1961).
71. M. L. Khidekel', A. G. Khrushch, and A. A. Balandin, Dokl. Akad. Nauk SSSR, 189, 1389 (1965).
72. A. Ohno and N. Kito, Chem. Lett., No. 3, 369 (1972).
73. A. Ohno, T. Kimura, S. Oka, and V. Ohnishi, Tetrahedron Lett., No. 8, 757 (1978).
74. R. J. Kill and D. A. Widdowson, J. Chem. Comm., No. 19, 755 (1976).
75. M. V. Nekhoroshev and O. Yu. Okhlobystin, Zh. Org. Khim., 13, 126 (1977).
76. V. V. Ershov, N. A. Volod'kin, A. I. Prokof'ev, and V. P. Solodovnikov, Usp. Khim., 42, 1622 (1973).
77. N. T. Berberova, A. A. Bumber, M. V. Nekhoroshev, V. B. Panov, and O. Yu. Okhlobystin, Dokl. Akad. Nauk SSSR, 246, 108 (1979).
78. Z. M. Hashish and J. M. Hoodless, Can. J. Chem., 54, 2261 (1976).
79. R. A. Hood, R. H. Prince, and K. A. Robinson, Chem. Commun., No. 7, 300 (1978).
80. N. T. Ioffe, L. Yu. Yuzefovich, and V. G. Mairanovskii, Teor. Eksp. Khim., 40, 1729 (1971).
81. A. L. Buchachenko and G. M. Zhidomirov, Usp. Khim., 40, 1729 (1971).
82. A. S. Morkovnik and O. Yu. Okhlobystin, Usp. Khim., 48, 1968 (1979).
83. C. E. H. Bawn and D. Verdin, Trans. Faraday Soc., 56, 815 (1960).
84. V. D. Pokhodenko, A. A. Beloded, and V. G. Koshechko, Redox Reactions of Free Radicals [in Russian], Naukova Dumka, Kiev (1977), p. 58.
85. N. I. Buran, S. P. Ponamarenko, and A. A. Yasnikov, Dokl. Akad. Nauk Ukr. SSR, No. 2, 326 (1978).
86. I. M. Sosonkin, V. A. Subbotin, V. N. Charushin, and O. N. Chupakhin, Dokl. Akad. Nauk SSSR, 229, 888 (1976).
87. É. G. Rozantsev and V. D. Sholle, Organic Chemistry of Free Radicals [in Russian], Khimiya, Moscow (1979), p. 37.
88. V. D. Pokhodenko, V. A. Khizhnyi, V. P. Koshechko, and O. I. Shkrebtii, Dokl. Akad. Nauk SSSR, 210, 640 (1973).
89. V. G. Koshechko, V. A. Khizhnyi, and V. D. Pokhodenko, Zh. Org. Khim., 11, 903 (1975).

90. A. A. Medzhidov, É. G. Rozantsev, and M. B. Neiman, Dokl. Akad. Nauk SSSR, 168, 248 (1966).
91. A. L. Buchachenko and A. M. Vasserman, Free Radicals [in Russian], Khimiya, Moscow (1973), p. 404.
92. O. M. Polumbrik, G. F. Dvorko, and É. A. Ponomareva, Zh. Org. Khim., 8, 2417 (1972).
93. É. A. Ponomareva, O. M. Polumbrik, and E. I. Zaika, Zh. Org. Khim., 7, 1512 (1971).
94. G. F. Dvorko, L. S. Degtyarev, and A. K. Tomanshchik, Dokl. Akad. Nauk SSSR, 202, 1073 (1972).
95. O. M. Polumbrik, G. F. Dvorko, and O. M. Grishin, Ukr. Khim. Zh., 37, 167 (1971).
96. O. M. Polumbrik, E. I. Zaika, and G. F. Dvorko, Zh. Org. Khim., 10, 1953 (1974).
97. U. Fisher, M. Sadeghi, and W. H. Hambright, Tetrahedron Lett., No. 3, 303 (1978).
98. G. D. Tirzit and G. Ya. Dubur, Khim. Geterotsikl. Soedin., No. 1, 133 (1972).
99. J. J. G. Cadogan and A. G. Ravley, Chem. Commun., No. 5, 179 (1974).
100. M. E. Vol'pin, L. V. Savitskii, T. N. Novodarova, and E. M. Kolosova, Izv. Akad. Nauk SSSR, Ser. Khim., No. 7, 1498 (1977).
101. M. E. Vol'pin, A. F. Mironov, T. N. Novodarova, E. M. Kolosova, and V. A. Ioffe, Izv. Akad. Nauk SSSR, Ser. Khim., No. 1, 175 (1980).
102. M. E. Vol'pin, V. M. Berezovskii, T. N. Novodarova, T. A. Melent'eva, E. M. Kolosova, N. S. Genokhova, and T. A. Lebedeva, Izv. Akad. Nauk SSSR, Ser. Khim., No. 10, 2231 (1977).
103. K. B. Yatsimirskii, Yu. I. Bratushko, I. A. Zatsny, E. E. Kriss, and G. T. Kurbatova, Zh. Neorg. Khim., 22, 2441 (1977).
104. N. M. Émanuél', Chain Reactions of Liquid-Phase Oxidation of Hydrocarbons [in Russian], Nauka, Moscow (1965), p. 21.
105. I. B. Afanas'ev, Usp. Khim., 48, 97 (1979).
106. Y. Sato, H. Kojima, and H. Shirai, Tetrahedron, 30, 2695 (1974).
107. V. B. Panov, M. V. Nekhoroshev, and O. Yu. Okhlobystin, Dokl. Akad. Nauk SSSR, 249, 622 (1979).
108. A. F. Pozharskii, Khim.-farm. Zh., No. 1, 34 (1976).
109. O. Dimrot and H. Roos. Ann. Chem., 456, 177 (1927)
110. Y. Ohnishi and T. Numakunae, Tetrahedron Lett., 31, 2699 (1976).
111. Y. Ohnishi, M. Kagami, and A. Ohno, J. Am. Chem. Soc., 97, 4766 (1975).
112. M. E. Vol'pin, Z. N. Parnes, and D. N. Kursanov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, No. 5, 950 (1960).
113. H. Volz and L. M. Volz, Tetrahedron Lett., 4683 (1966).
114. H. Volz and H. W. Schnell, Angew. Chem., 77, 846 (1965).
115. D. H. Geske, J. Am. Chem., 81, 4145 (1959).
116. Ya. P. Stradyn', Ya. R. Uldrikis, Yu. I. Beilis, G. Ya. Dubur, and P. É. Sausin', and A. G. Chekavichus, Khim. Geterotsikl. Soedin., No. 11, 1525 (1975).
117. Ya. P. Stradyn', G. Ya. Dubur, and Ya. R. Uldrikis, Khim. Geterotsikl. Soedin., No. 1, 84 (1972).
118. Ya. V. Ogle, Ya. P. Stradyn', and G. Ya. Dubur, Khim. Geterotsikl. Soedin., No. 9, 1963 (1980).
119. Ya. P. Stradyn', Yu. I. Beilis, G. Ya. Dubur, and T. L. Slonskaya, Izv. Akad. Nauk Latv. SSSR, Ser. Khim., No. 3, 373 (1978).
120. I. M. Sosonkin, O. N. Chupakhin, and A. I. Matern, Zh. Org. Khim., 15, 1976 (1979).
121. E. Sturn, H. Kiesele, and E. Daltrozzo, Chem. Ber., 111, 227 (1978).
122. O. N. Chupakhin, I. M. Sosonkin, A. I. Matern, and G. N. Strogov, Dokl. Akad. Nauk SSSR, 250, 879 (1980).
123. E. T. McNamara, J. W. Nief, and J. F. Ambrose, J. Org. Chem., 42, 988 (1977).
124. G. Ya. Dubur, Yu. I. Beilis, E. M. Belash, and A. E. Sausin', in: Seventh All-Union Conference on Polarography [in Russian], Nauka, Moscow (1978), p. 51.
125. S. F. Nelsen, E. L. Clennan, L. Echegoyan, and L. A. Crezzo, J. Org. Chem., 43, 2622 (1978).
126. F. M. Martens, J. W. Verhoeven, R. A. Gase, U. K. Pandit, and Th. J. Boer, Tetrahedron, 34, 443 (1978).
127. I. M. Sosonkin, in: The Development of Organic Synthesis on the Basis of a Study of the General Principles and Mechanisms of the Reactions of Organic Chemistry [in Russian], Nauka, Leningrad (1980), p. 9.
128. I. M. Sosonkin, A. Ya. Kaminskii, S. S. Gitis, V. A. Subbotin, and T. K. Polynnikova, Zh. Org. Khim., 9, 1470 (1973).
129. Ya. P. Stradyn', in: Polarography in Organic Chemistry [in Russian], Khimiya, Leningrad (1975), p. 102.

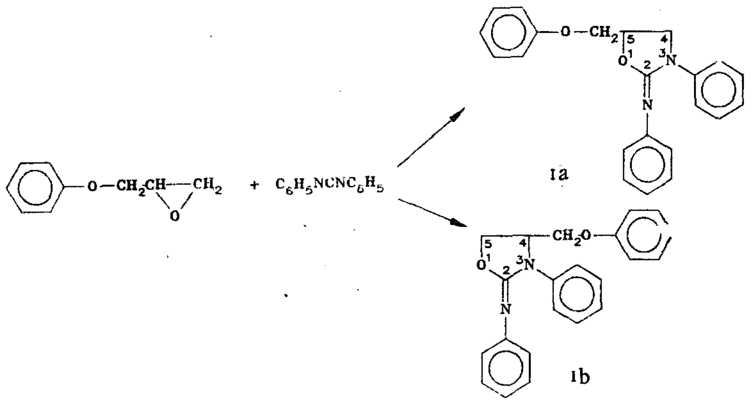
130. O. Yu. Okhlobystin and N. T. Berberova, in: Advances in the Electrochemistry of Organic Compounds [in Russian], Novocherkassk (1980), p. 11.
131. O. Yu. Okhlobystin, in: Radical Ions in Electrode Processes [in Russian], Nauka, Moscow (1983), p. 57.

X-RAY CRYSTALLOGRAPHIC INVESTIGATION OF 2-N-PHENYLIMINO-3-PHENYL-5-PHENOXYMETHYL-1,3-OXAZOLIDINE

G. V. Gridunova, V. E. Shklover,
Yu. T. Struchkov, A. M. Fainleib,
Ts. M. Frenkel', and V. A. Pankratov

UDC 548.737:547.787.1

Earlier [1] substituted 2-N-phenyliminooxazolidine (I) was synthesized by the reaction of diphenylcarbodiimide with phenylglycidyl ether. On the basis of the data of elementary analysis, the IR, PMR, and mass spectra, hydrolysis of the reaction product, which led to 2-oxazolidinone, and countersynthesis of the latter, the structure (Ia) with phenyl and phenoxymethyl substituents in the 3- and 5-positions, respectively, was proposed for compound I. However, these data did not exclude the possibility of the formation of the isomeric 3-phenyl-4-phenoxymethyl-2-N-phenylaminooxazolidine (Ib) in this reaction was well:



An x-ray crystallographic investigation that we conducted for an unambiguous establishment of the structure of compound I and analogous heterocyclic fragments of thermostable polymers confirmed the proposed structure of the compound as Ia.

The central oxazolidine ring is noncopolanar. The parameters of folding $q_2 = 0.333$ Å and $\varphi_2 = 351.4°$, calculated by the Kramer—Pople method [2], characterized its conformation as intermediate between an envelope and a half-chair. The $C_{(5)}$ and $C_{(4)}$ atoms emerge -0.274 and 0.109 Å on different sides of the P_1 plane of the other three atoms of the heterocycle (Table 1).

The length of the $C_{(4)}-C_{(5)}$ bond 1.525 (6) Å is close to the standard length of the single bond $C(sp^3)-C(sp^3)$ 1.537 Å [3]. The $C_{(5)}-O_{(1)}$ bond 1.448 (4) Å is slightly lengthened, while the $C_{(4)}-N_{(3)}$ bond 1.447 (5) Å is appreciably shortened in comparison with the corresponding standard bond lengths $C(sp^3)-O$ 1.426 Å and $C(sp^3)-N$ 1.472 Å [3]. On the whole, the distribution of the bond lengths in the oxazolidine ring of compound I corresponds to that observed in the related 3,5-substituted oxazolidinones [4-6], with the exception of a small lengthening of the $C_{(2)}-O_{(1)}$ bond to 1.377 (5) Å in comparison with 1.350 Å (average for nine derivatives of 3,5-oxazolidinone [4-6]) and 1.356 Å (in unsubstituted 2-oxazolidinone [7]). The endocyclic valence angles in the heterocycle I agree with those observed in oxazolidinone analogs [4-6]. A comparison of the geometry of the rings in compound I and the above-mentioned analogs and derivatives of oxazolidine, all the carbon atoms of the ring of which are sp^3-hy-

---

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Moscow 117813. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1026-1031, August, 1984. Original article submitted December 14, 1983.

0009-3122/84/2008-0831$08.50