Chemistry of Heterocyclic Compounds, Vol. 40, No. 5, 2004

OXIDATION OF HETEROCYCLIC COMPOUNDS BY PERMANGANATE ANION. (REVIEW)

A. T. Soldatenkov, A. V. Temesgen, and N. M. Kolyadina

Data on the oxidative transformations of heterocyclic compounds with permanganate anion are reviewed.

Keywords: permanganate anion, oxidation.

The oxidation reactions of organic compounds make up one of the most important regions of chemistry, the principal objective of which is the synthesis of oxygen-containing substances. Among the various oxidizing agents currently used in synthesis [1, 2] the most widespread are manganese compounds, which make it possible both to introduce oxygen-containing functions into the initial molecules and to realize dehydrogenation, aromatization, decyclization, cyclization, and coupling reactions. The literature on the use of the variable-valence compounds of manganese in organic synthesis, and this includes reviews, is very comprehensive [3-10], and a considerable proportion of it has been devoted to the oxidation of organic substances by permanganates.

Potassium permanganate, as the most readily available of these reagents, is most often used for oxidation. Apart from this compound, however, it is also possible to use the sodium, copper(II), magnesium, silver, zinc, and ammonium salts. On account of their suitable solubility in organic solvents tetraalkylammonium, benzyltrialkylammonium, and triarylphosphonium permanganates make it possible to oxidize substrates in nonaqueous media [2, 7].

Analysis of the literature shows that there are hardly any reviews that deal systematically with the oxidation of heterocyclic compounds in the presence of permanganates. In order to fill this gap the present review was undertaken in order to analyze research of the last 15-20 years on the main types of controlled oxidative transformation of heterocyclic compounds under the influence of the permanganate anion. Transformation of side substituents in the heterocycle, the production of oxo groups at the ring atoms, the dihydroxylation of partially hydrogenated heterocycles, dehydrogenation and aromatization, oxidative coupling, and decyclization and the formation of heterocycles are discussed.

1. TRANSFORMATIONS OF SIDE SUBSTITUENTS IN HETEROCYCLES

This section contains data on oxidative transformations in alkyl, alkenyl, hydroxyalkyl, formyl, and thiol groups present in the initial heterocyclic compounds.

During oxidation of 5-methyl-substituted 2-(2-benzimidazolyl)furan **1** in the $KMnO_4$–H_2O system (30°C, 1.5 h) it is possible to obtain the corresponding furancarboxylic acid with a 21% yield only in the form of

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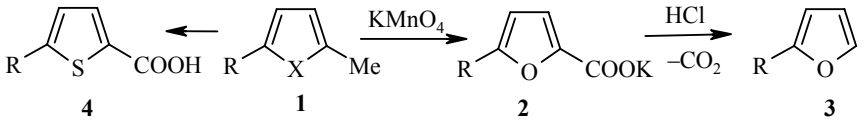
Russian Peoples' Friendship University, Moscow; e-mail: nKolyadina@sci.pfu.edu.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 643-669, May, 2004. Original article submitted October 4, 2000.

the potassium salt **2**, since acidification leads to complete decarboxylation [11]. (The yield of the furan **3** amounted to 44%.) At the same time the thienyl derivative **1** (X = S, 80°C) is converted into the stable free acid **4** (yield 27%).

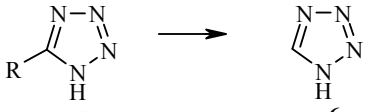


4 **1** **2** **3**

X = O, S; R = 1-methyl-2-benzimidazolyl

Methyl groups in the triazole rings of bis-1,2,4-triazolo[3,4-*d*]-1,2,4-triazolo[3,4-*f*]furazano[3,4-*b*]-pyrazines are oxidized to carboxyl groups by the action of potassium permanganate in aqueous solutions [12].

In certain cases dealkylation of the alkyl-substituted heterocycles is observed under the conditions of oxidation, and this makes it possible to synthesize the unsubstituted heterocycles. For example, the methyl and dimethylaminoethyl group at position 5 of the tetrazoles **5** undergo oxidative cleavage on heating with potassium permanganate (60-98°C) [13, 14]. This reaction is recommended as a convenient method for the production the un substituted tetrazole **6**.

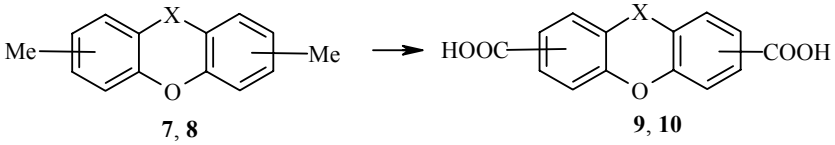


5 **6**

5 R = Me; $Me_2NCH_2CH_2$

The methyl group in 2-halopicoline N-oxides is oxidized to carboxyl, and the presence of the halogen reduces the resistance of the heterocycle to oxidation [15]. The oxidation of 5,5'-dimethyl-2,2'-bipyridine gave a carboxylic acid that had a powerful inhibiting effect on the propylhydroxylase responsible for the deposition of collagen in the human organism [16].

On heating potassium permanganate oxidizes the dimethyl-substituted xanthones **7** [17] or phenoxaphosphine 10-oxides **8** [7] with the formation of dicarboxylic acids **9** or **10**. According to data in [18], the methyl group in the 6-methyluracil derivative is not oxidized by aqueous potassium permanganate. Instead of the expected carboxylic acid the N-oxide of the iminol tautomer of the initial substrate was isolated.

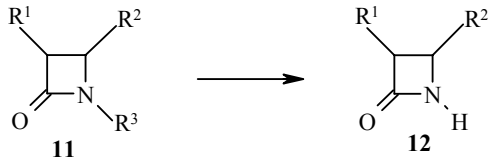


7, **8** **9**, **10**

7, **9** X = C=O, **8**, **10** X = O=P–Ph

The methylene group in bis(2-benzodiazolyl)methanes is oxidized by potassium permanganate to a secondary alcohol and/or ketone group [19].

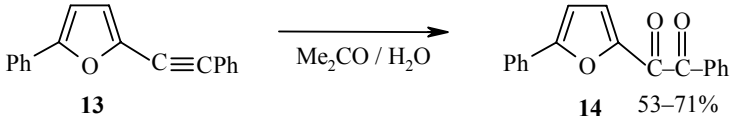
During study of the transformations of alkenyl substituents at the nitrogen atom in β-lactams **11** it was established that they are eliminated under very mild conditions with the formation of the N-unsubstituted heterocycle **12** [20].



11 **12**

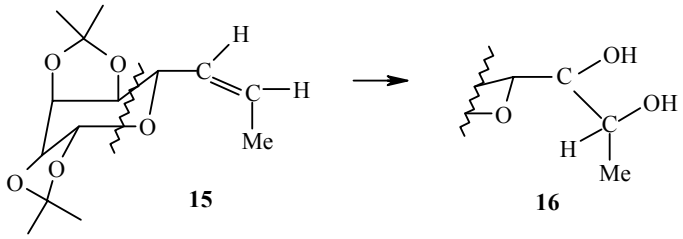
R^1 = OPh; R^2 = Ph; R^3 = $CH{=}CH_2$, CH=CHMe

2-Phenyl-5-phenylethynylfuran **13** is oxidized by potassium permanganate with a satisfactory yield to the dicarbonyl derivative **14** [1].



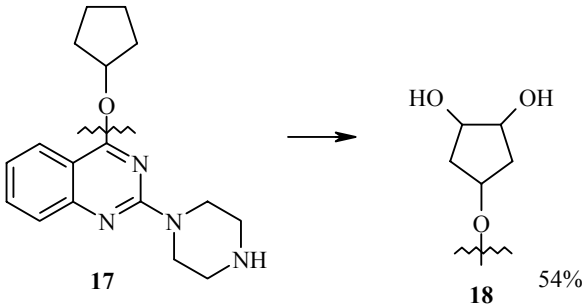
13 **14** 53–71%

The hydroxylation of the *cis*-tetrahydropyranyl-substituted alkene **15** was realized [21]. It is assumed that the double bond is attacked by the electrophilic permanganate from the side opposite to the pyran ring, in which the $C_{(5)}$–O bond must be in the *s-cis* conformation in order to form the single glycol **16**.



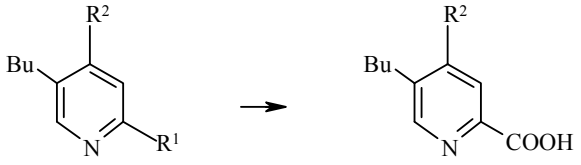
15 **16**

In [22] the O-cyclopentenyl fragment in the hydroxyquinazoline **17** was successfully hydrogenated with potassium permanganate in the THF–H_2O–KOH system. The obtained 4-(*trans*-3,*trans*-4-dihydroxycyclopentan-*r*-yloxy)quinazoline **18** and its quaternary salts were promising as anticancer agents.



17 **18** 54%

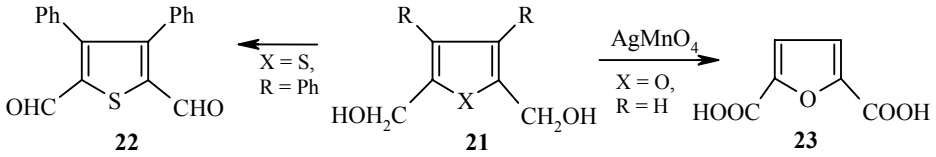
During synthesis of the antibiotics fuzarinic acid and its analogs **19** potassium permanganate was used for oxidation of the α-styryl group to a carboxyl group in the pyridines **20** without affecting the *n*-butyl substituent at the $C_{(5)}$ atom [23].



20 **19**

R^1 = CH=CHPh, CH_2OH; R^2 = H, Me, NO_2, OMe, Cl

If bis(pyridine)silver permanganate is used hydroxymethyl groups can be oxidized to carbaldehyde groups [2]. Thiophene-2,5-dimethanol was converted quantitatively by this reagent into the dialdehyde **22** [24]. During an attempt at the analogous oxidation of furan-2,5-dimethanol, however, furan-2,5-dicarboxylic acid **23** was isolated with a yield of 56%. Hydroxymethyl substituents in xanthones of type **7** [17] and in pyridines **20** [23] are converted into carboxyl groups by the action of potassium permanganate.



22 **21** **23**

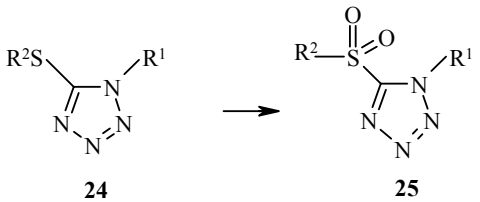
The 1-hydroxyethyl group in 1,2,3-1H-benzotriazoles was oxidized into a hydroxycarbonylmethyl group (potassium permanganate in aqueous acetic acid) [25]. The benzotriazolylacetic acids obtained here exhibit herbicidal characteristics.

The oxidation of carbaldehyde substituents to carboxyl groups takes place particularly readily. Thus, an almost quantitative yield of 2-furancarboxylic acid is obtained during the oxidation of furfural with permanganate anion generated in a diaphragm-free electrochemical cell from an alkaline solution of manganese dioxide [26].

In the case of the oxidation of 2-pyrrolecarbaldehyde with potassium permanganate in aqueous acetone at 40°C the yield of the corresponding acid amounted to 69% [27]. When the reaction temperature was reduced to 25°C the oxidation rate decreased by 2.5 times, and when the temperature was raised above 40°C decarboxylation occurred. It is also possible to obtain the corresponding hetarenecarboxylic acids with yields of 58-90% by the analogous oxidation of 2-formylthiophene [28], 3-formylindole [29], 3-formyl-β-carbolin [30], and 3-quinolinecarbaldehyde [31, 32].

2-Nitrophenylthio-substituted benzimidazoles and benzothiazoles were oxidized to their sulfonyl derivatives with good yields with the aim of producing antimicrobial agents [33].

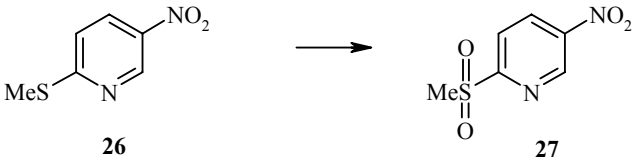
A series of 5-alkylthio- and arylthiotetrazoles **24** were converted into the corresponding sulfonyl derivatives **25** by oxidation under the conditions of phase-transfer catalysis (tetrabutylammonium bromide–chloroform–aq. acetic acid) [34, 35]. In the case of R^1 = H and R^2 = Ph only the disulfide is formed.



24 **25**

R^1 = H, Me, Et, CH_2Ph; R^2 = Me, Et, *n*-Bu, CH_2Ph, C_6H_4Me-*p*, $C_6H_4NO_2$-*m*

In the synthesis of activated haptenes, which are used in the production of monoclonal antibodies, potassium permanganate is effective for oxidation of the sulfide side group in the pyridine **26** to methylsulfonyl (aqueous acetic acid). The yield of the sulfone **27** amounted to 87% [36].



26 **27**

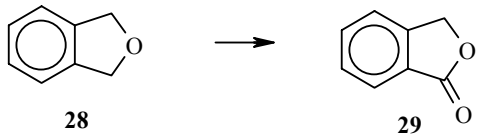
Arylthio groups in benzo[*f*]quinolines are oxidized by a 1% aqueous solution of potassium permanganate to the corresponding sulfones, which were tested as antibacterial agents [37]. Alkylthio groups in 1,5-naphthiridines and arylthio groups in uracils [33] were converted by the potassium permanganate/acetic acid system into sulfonyl groups.

According to data in [38], sulfenamide groups in 1,2,4-triazole are successfully oxidized to sulfonamide groups. A similar synthesis was realized with the aim of studying the inhibition of anhydrases and reducing ocular pressure.

A series of heterocyclic bissulfonamides, which proved to be good inhibitors of zinc-containing anhydrases, were synthesized by analogous oxidation [39].

2. THE FORMATION OF OXO GROUPS AT THE RING ATOMS OF A HETEROCYCLE

In a number of cases potassium permanganate deposited on aluminum oxide secures high selectivity of oxidation and simplifies isolation of the products. 1,3-Dihydrobenzofuran **28** is easily oxidized to the lactone **29** by this reagent [40].

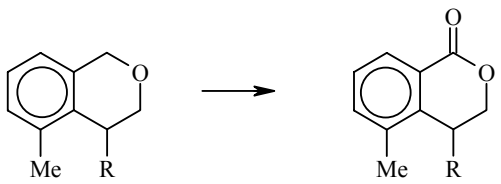


28 **29**

91%

At the same time its isomer 2,3-dihydrobenzofuran was found to be stable under these conditions even during prolonged oxidation (up up to 217 h).

In an analogous system derivatives of benzopyran **30** and dibenzopyran **31** are converted with high yields into the lactone **32** [41] and the ketone **33** [40] respectively.

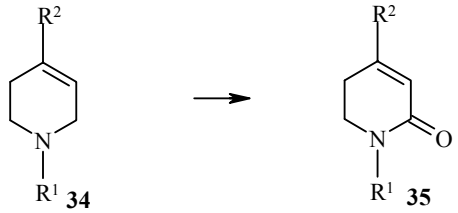


30 **32**

R = H, Me, Et, CH_2Ph

31 **33**

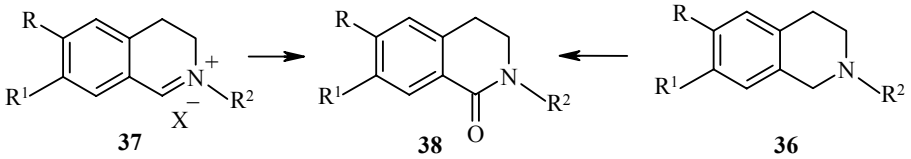
1,4-Disubstituted tetrahydropyridines **34** were converted into the unsaturated lactams **35** by the brief action of aqueous potassium permanganate in acetonitrile at 20°C [42-44].



34 **35**

R^1 = Me, CH_2Ph, $CH_2C_6H_4Cl$-*p*; R^2 = Ph, 4-Py, CH=CHPh

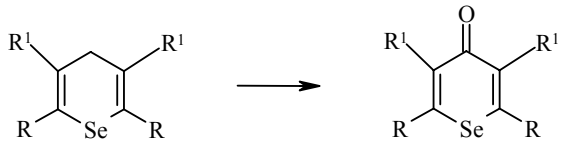
The N-acetyltetrahydroisoquinolines **36** and the quaternary salts of dihydroisoquinolines **37** were oxidized with good yields to tetrahydro-1-isoquinolinones **38** by potassium permanganate under the conditions of phase-transfer catalysis (crown ether) [45]. Isoquinolinium and quinolinium quaternary salts are also converted into the corresponding N-substituted 1-isoquinolones and 2-quinolones.



37 **38** **36**

R, R^1 = H, OMe, NO_2 ; R^2 = Me, Et, CH_2Ph, COEt, COMe, COPh, CHO

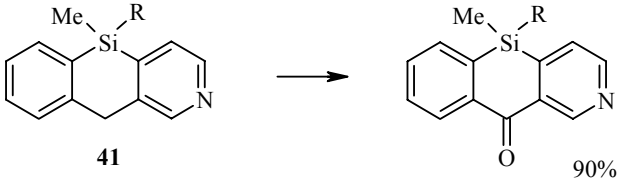
It was found that 4H-selenopyrans **39** are easily oxidized by potassium permanganate (heating in acetone/acetonitrile) to γ-selenopyrones **40** (yields 45-65%) [46].



39 **40**

R = Ph; R^1 = H, Me

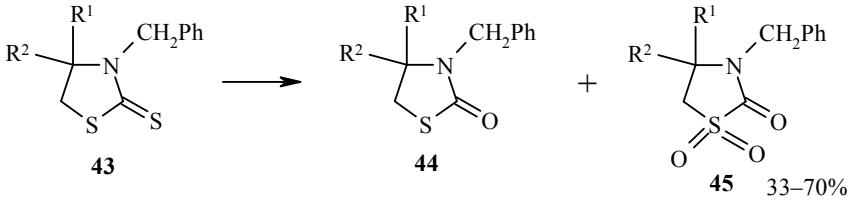
Silaazaanthracenes **41** are oxidized with high yields by potassium permanganate in acetone at 20°C to silaazaanthrones **42** [47].



41 **42** 90%

R = Ph, Me

In [48, 49] a series of 2-thiazolidinethiones **43** were oxidized with potassium permanganate to thiazolidinones **44** and their S,S-dioxides **45** under the conditions of phase-transfer catalysis. The authors note a marked increase in the effectiveness of oxidation to the dioxides **45** if benzoic acid is added to the reaction mixture.



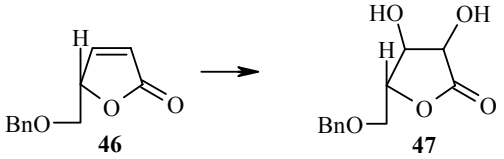
43 **44** **45** 33–70%

R^1 = H, Et; R^2 = H, CH_2Ph, *i*-Pr

3. DIHYDROXYLATION OF PARTIALLY HYDROGENATED HETEROCYCLES

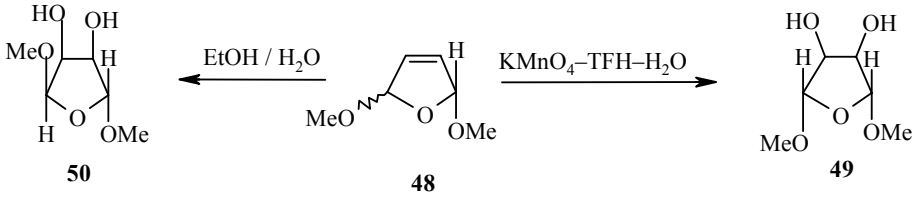
Aqueous solutions of potassium permanganate were used for the dihydroxylation of partially reduced heterocycles containing a C=C double bond (the Wagner method). The reaction is usually conducted in the cold in a neutral or weakly alkaline medium, while the *cis*-1,2-diols are formed with moderate yields. Oxidation in an acidic medium or without cooling often leads to the products from more profound transformations.

3,4-Dehydrobutyrolactone **46** is converted with a good yield into the 3,4-dihydroxylactone **47**, in which the *cis* isomer is formed with 60% selectivity [50].



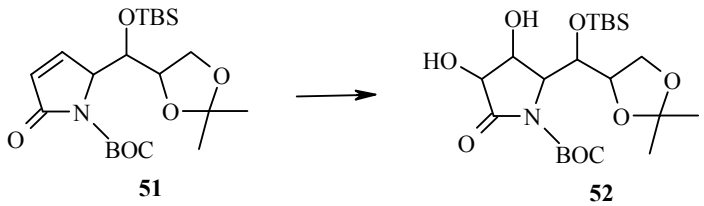
46 **47**

It was established that in aqueous THF only *cis*-2,5-dimethoxy-2,5-dihydrofuran (**48**) undergoes dihydroxylation, giving the product **49** [1, 51]. The *trans* isomer **48** only forms the diol **50** if the THF is replaced by ethanol.



50 **48** **49**

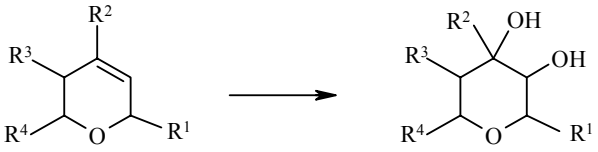
Oxidation of the unsaturated five-membered lactam **51** in the $KMnO_4$–18-crown-6–CH_2Cl_2 system gives the diol **52** with a yield of 65% [52].



51 **52**

TBS = tert-butyldimethylsilyl, BOC = tert-butoxycarbonyl

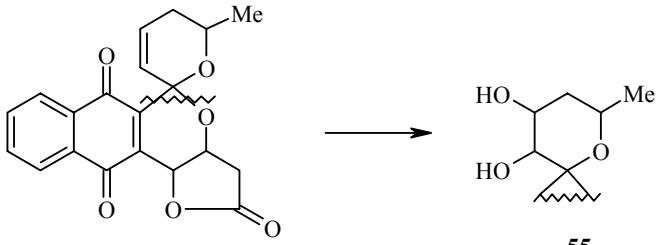
The Wagner reaction was used successfully for the *cis* dihydroxylation of the dihydropyrans **53** (in a neutral medium) [53-55]. The ratio of the diastereomeric glycols **54** is determined by the nature of the substituent R^1.



53 **54**

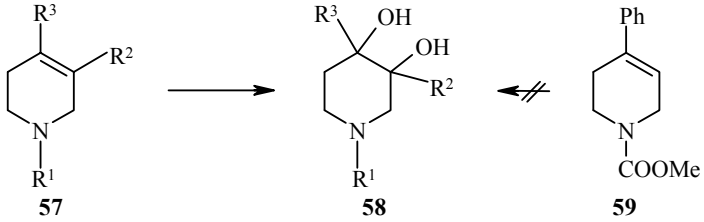
R^1 = H, Me, CH_2Ac, OMe, OEt, OCH_2Ph, $NHCOOEt$;
R^2 = H, Me; R^3 = H, OAc; R^4 = H, Me, CH_2OH, $CONH_2$, OMe, OAc

In the synthesis of analogs of the antibiotic griseusin **55** cetyltrimethylammonium potassium permanganate was used successfully for the *cis* dihydroxylation of the spirofused dihydropyran ring in the initial compound **56** (20°C, 3 h) [56].



56 **55**

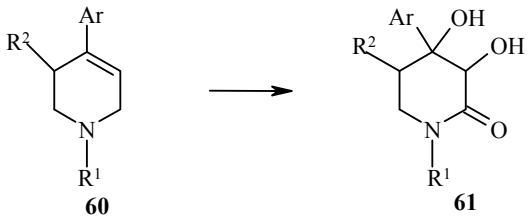
The N-alkoxycarbonyltetrahydropyridines **57** are dihydroxylated smoothly by an aqueous solution of potassium permanganate in the cold to the diols **58** [57]. However, the simultaneous presence of two methyl groups at the double bond or replacement of the N-alkoxycarbonyl substituent by an N-methyl greatly reduces the yield of the diols (by two or more times). The introduction of a phenyl radical at the $C_{(4)}$ atom completely deactivates the piperideine ring in compound **59**.



57 **58** **59**

R^1 = COOMe, COOEt, Me; R^2, R^3 = H, Me

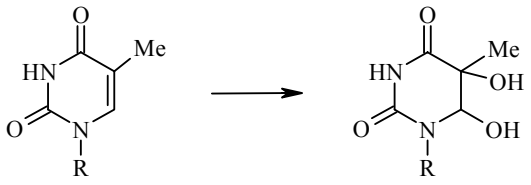
It was later established [58-61] that a slight modification of the conditions for the Wagner reaction (its realization not in the cold but at 25-35°C) activates the 4-arylpiperideines **60**. Here, however, the latter are converted not into the expected piperidinediols but into the dihydroxylactams **61**. It was found that this oxohydroxylation reaction takes place through preliminary oxidation of the initial tetrahydropyridines **60** to their 2-oxo derivatives, which are then easily dihydroxylated [44, 62].



60 **61**

R^1 = Me, Et, CH_2Ph; R^2 = H, CH_2OAc; Ar = Ph, 4-Py

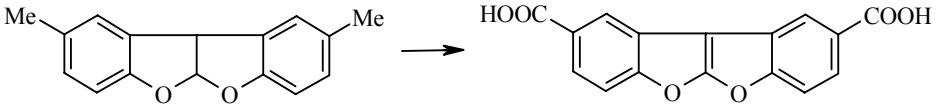
During the action of potassium permanganate on oligonucleotides or on DNA (**62**, where R is the nucleotide or DNA residue) under mild conditions it was established that of all the purine and pyrimidine bases only thymine reacts selectively, being converted into the *cis*-glycol of dihydrothymine **63** [63].



62 **63**

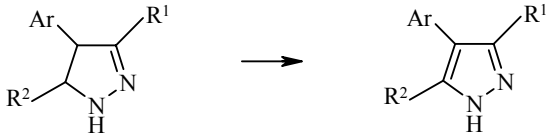
4. DEHYDROGENATION AND AROMATIZATION OF HETEROCYCLES

The permanganate ion has found fairly widespread use in the chemistry of heterocyclic compounds as a dehydrating and aromatizing agent. Thus, with potassium permanganate 2,9-dimethyldihydrodibenzofuran **64** undergoes dehydration with simultaneous oxidation of the methyl groups to carboxyl groups [64]. With phenylenediamine the obtained diacid **65** forms a highly heat-resistant polymer.



64 **65**

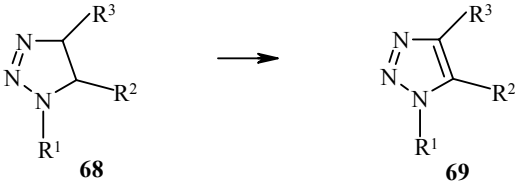
The substituted pyrazolines **66** are converted by potassium permanganate into good yields of the corresponding pyrazoles **67** [65].



66 **67**

Ar = Ph, C_6H_4Me-*p*; R^1, R^2 = COPh, COC_6H_4Me-*p*, COC_6H_4OMe-*p*, COOEt

The substituted triazolines **68** readily undergo aromatization with potassium permanganate in the presence of phase-transfer catalysts. The yields of the triazoles **69** were 50-70% [66].

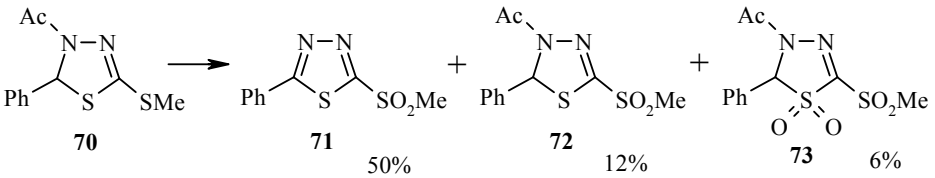


68 **69**

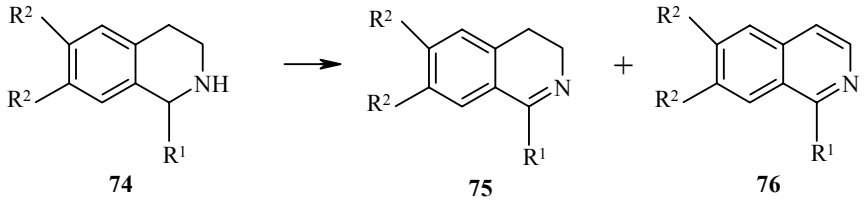
R^1 = Me, C_6H_4Cl-*p*, C_6H_4Me-*p*, R^2 = 4-Py, 2-quinolyl, COOEt, R^3 = H, Me, Ph

In [67] it was established that the diazoline **70** is oxidized by potassium permanganate in acetic acid at room temperature after only 1 h. The main reaction path here is aromatization of the heterocycle to compound **71** as a result of removal of the N-acetyl group and dehydrogenation. The structure of the minor products **72** and

73 makes it possible to assume that oxidation of the thiomethyl side group to sulfonyl occurs at the first stage. Similar results were obtained with the introduction of various substituents (Me, OMe, Cl, CN, NO_2) at the *para* position.

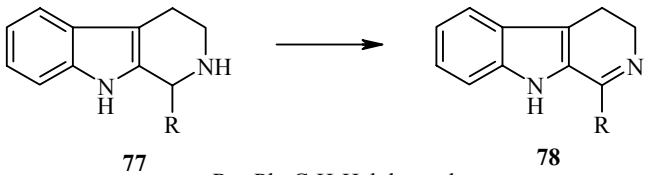


Under the influence of potassium permanganate tetrahydropyridine fragments may be converted into their dihydro derivatives or are fully aromatized. Thus, 3-hydroxymethyl-1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine is oxidized with removal of the hydroxymethyl and N-methyl groups to 4-phenylpyridine (yield 10%) [61]. It was established that oxidation of the unsubstituted 1,2,3,4-tetrahydroisoquinoline by potassium permanganate in acetone or acetonitrile at 20°C is a fast exothermic aromatization reaction, leading after 20 min to isoquinoline (yield 50%) [45]. At 0°C, however, dehydrogenation of the tetrahydroisoquinolines **74** occurred after a few minutes with the formation of a mixture of 3,4-dihydroisoquinolines **75** (yield 80%) and isoquinolines **76** (yield 20%). If catalytic amounts of 18-crown-6 were used high selectivity in the dihydroisoquinoline was achieved.



R^1 = H, Ph, $C_6H_4NO_2$-*p*, R^2 = H, OMe

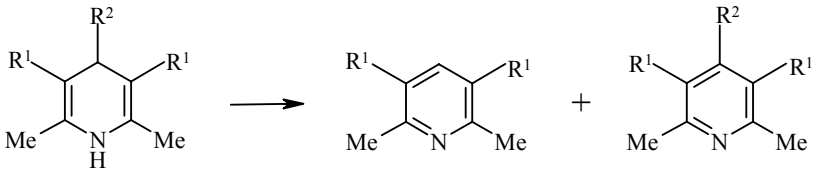
In dry THF potassium permanganate can have a mild dehydrating effect. Thus, 1,2,3,4-tetrahydrocarbolins **77** are transformed selectively into the 3,4-dihydro derivatives **78** with yields of 28-94%. In some cases the nature of the substituent at the $C_{(1)}$ atom gives rise to complete aromatization of the heterocyclic fragment [68].



R = Ph, C_6H_4Hal, hetaryl

Potassium permanganate has also been used satisfactorily in the aromatization of N-unsubstituted 1,4-dihydropyridines [70, 71] in addition to the oxidation agents such as HNO_3, CrO_3, MnO_2, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone usually employed for this purpose [69]. The oxidative aromatization of 1,4-dihydropyridines **79** by the action of potassium permanganate under various conditions was studied in detail in [71]. Thus, boiling of Hantsch esters in dry benzene in the presence of potassium permanganate deposited on montmorillonite led only to the dealkylation products **80**, while in the case of 4-aryl substituents only the 4-substituted pyridines **81** were formed. The use of moist benzene under analogous conditions gave a mixture of compounds **80** and **81** in ratios between 1.0:1.5 and 1.5:1.0 (total yield 80-100%). Crown ethers and TEBAC

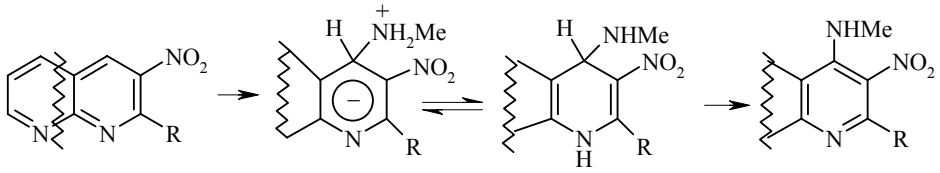
catalyze the oxidation with aqueous potassium permanganate also with the formation of a mixture of pyridines **80** and **81**. At the same time the oxidation of dihydropyridines with a solution of potassium permanganate in acetone or acetic acid is selective – only the pyridines **81** are formed (but with lower yields of 40-45%). Irradiation of the reaction mixture with ultrasound makes it possible to reduce the reaction time to a few minutes. The dealkylation–aromatization reaction presumably begins with homolytic cleavage of the N–H bond with transfer of a single electron to the pyridine ring. The alkyl radical at $C_{(4)}$ is then removed and dimerizes. Such a mechanism is confirmed by isolation of the dimerization product and also by successful oxidation of the initial dihydropyridines even with the use of small (catalytic) amounts of potassium permanganate. The dehydrogenation products **81** are formed by a concurrent ionic mechanism.



79 **80** **81**

R^1 = COOEt, R^2 = H, Et, *n*-Pr, *n*-Bu, Ph, $C_6H_4NO_2$-*p*, C_6H_4OMe-*p*

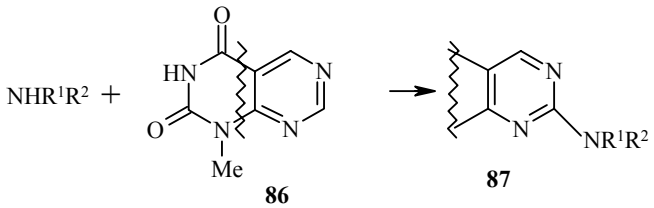
In the last 10-15 years a relatively new system containing liquid ammonia or alkylamine in mixture with potassium permanganate has been widely used for the introduction of an amino group into six-membered nitrogen heterocycles [72, 73]. Derivatives of pyridine [74, 75], quinoline [76], naphthiridines [77, 78], quinoxalines [79], and other azines [72, 73] enter into the reaction. It was established by NMR that nucleophilic addition of the ammonia or alkylamine to the heterocycle occurs at the first stage at a position determined not by the electron density but by the thermodynamic stability of the intermediate Meisenheimer σ adduct. The second stage involves oxidative dehydrogenation of the complex with generation of the aromatic system and the formation of amino- or alkylamino-substituted heterocycles. The sequence of transformations in 3-nitro-1,8-naphthiridines **82**, which are effectively aminated by methylamine at -7°C at position 4 through the complex **83** and the 1,4-dihydro derivative **84** with the formation of the methylaminonaphthiridines **85** [78], is presented below. In the case where R = Cl substitution of the halogen by the methylamino group is also observed.



82 **83** **84** **85**

R = H, NHPh, NHMe, NH_2, OH, OMe, Cl

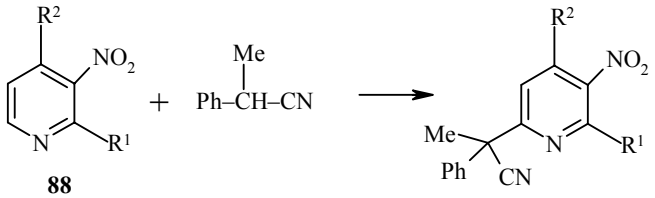
In [80] it was established that pyrimido[4,5-*d*]pyrimidine-2,4-dione **86** undergoes nucleophilic amination (at +7 to -75°C) mostly at position 7 with subsequent oxidation by potassium or silver permanganate to the amino derivatives **87** (yields 51-83%).



86 **87**

NR^1R^2 = NH_2, NHMe, NHEt, NHBu-*t*, piperidyl, morpholyl

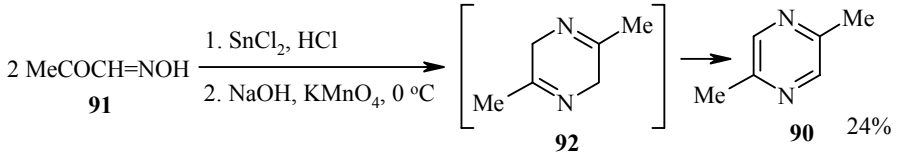
It was recently established that apart from amines the 2-phenylpropionitrile carbanion, generated *in situ*, can add to nitro-substituted pyridine **88** (and also thiophene, furan, pyrrole, and thiazole) rings in the NH_3–$KMnO_4$ system at -70°C [81]. The σ adducts formed here are then oxidized to the products from nucleophilic substitution of hydrogen **89**. Diphenylacetonitrile and triphenylacetonitrile only give the analogous substitution products with five-membered heterocyclic nitroarenes.



88 **89**

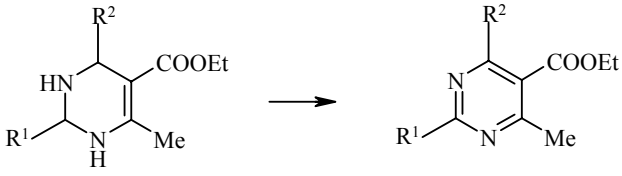
R^1 = H, Cl; R^2 = H, OEt

Potassium permanganate was used during the development of a one-pot method for the synthesis of 2,5-dimethylhydrazine **90** from hydroxyiminoacetone **91**, where its role involved oxidative dehydrogenation of the intermediate dihydropyrazine **92** [82].



91 **92** **90** 24%

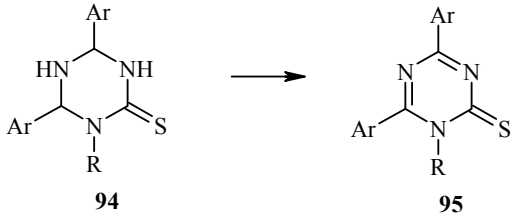
Full aromatization was observed during the oxidation of tetrahydropyrimidine **93** with potassium permanganate [83].



93

R^1 = $C_6H_4NO_2$-*o*; R^2 = $C_6H_4NO_2$-*m*

The tetrahydro-2-triazinethiones **94** are gently dehydrogenated by potassium permanganate to the corresponding triazinethiones **95** under the conditions of phase-transfer catalysis [84].



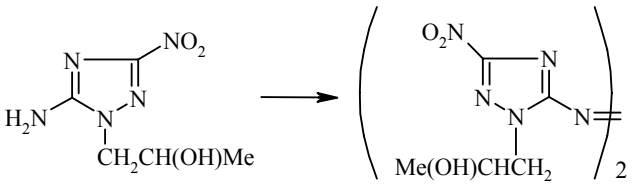
94 **95**

R = Me, Et; Ar = Ph, C_6H_4OMe-*p*

5. OXIDATIVE COUPLING

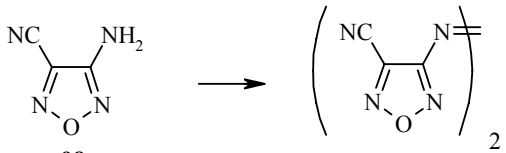
The permanganate anion has recently found use for various intermolecular condensations, which can be classified as N–N, C–N, and C–C oxidative coupling. Amino-substituted heterocycles having primary amino groups readily enter into N–N coupling with the formation of azo compounds. The, the oxidation of 1-aminoindole with potassium permanganate in an acidic medium gave azoindole [85]. The authors point out that the reaction path depends on pH inasmuch as deamination of the aminoindole is mainly observed in a neutral medium. An analogous azo product was isolated with a good yield during the oxidation of 5-aminopyrrolopyrimidine-2,4-dione.

3-Amino-5-nitro-1,2,4-triazole in the form of the potassium salt was converted by potassium permanganate into the high-energy stable azotriazole [86]. At 20°C in an acidic medium 5-amino-1-(2-hydroxypropyl)-3-nitro-1,2,4-triazole **96** is converted selectively into the azo compound **97** with a yield of 75% [87]. It was noted that the use of chromium(VI) oxide leads only to oxidation of the secondary alcohol group to ketone.



96 **97**

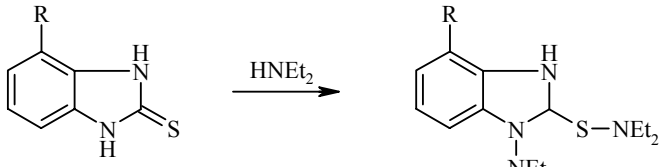
4-Amino-3-cyanofurazan **98** is transformed after 10 min (20°C) into the azafurazan **99** during oxidation with an aqueous solution of potassium permanganate [88]. In the case of 3,4-diaminofurazan trifurazans linked by azo bridges were synthesized [89]. Such high-energy molecules are of interest as a new type of potentially powerful explosive.



98 **99** 86%

A secondary cyclic amino group can also participate in N–N coupling under the influence of an oxidizing agent.

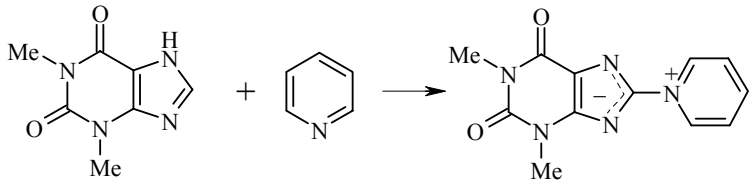
The possibility of oxidative N- and S-dialkylamination of benzimidazolinethiones **100** by diethylamine was demonstrated in [90].



100

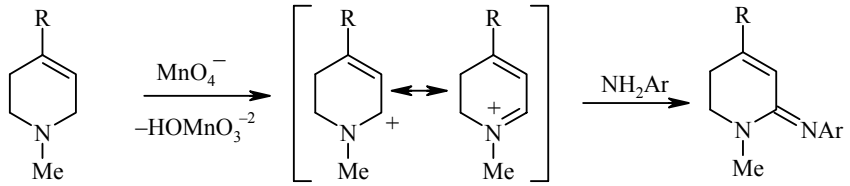
R = Me, Cl, NO_2

The condensation of pyridine with theophylline can be included among the C–N coupling reactions of heterocyclic compounds [91]. Oxidation of theophylline **101** with potassium permanganate was realized in a water–pyridine solution and led to the formation of the 8-pyridiniotheophyllinate **102**. It was stressed that this ylide is not formed in the absence of water.

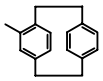


101 **102**

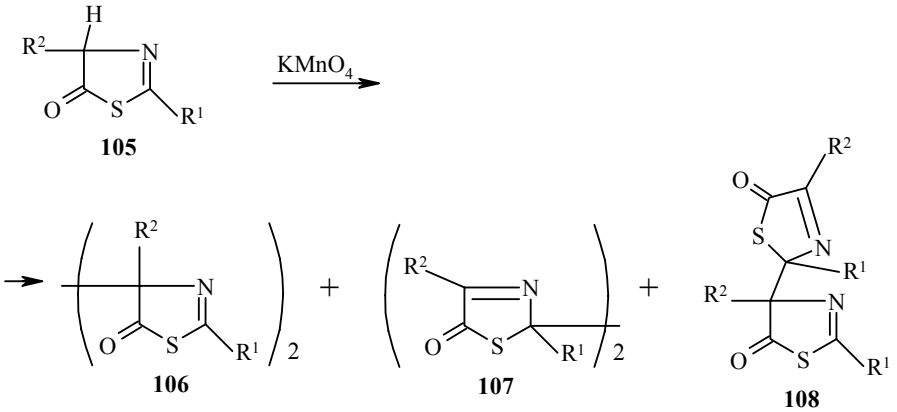
The intermolecular condensation of 4-aryl-1,2,3,6-tetrahydropyridines **103** with primary arylamines, leading to 2-aryliminotetrahydropyridines **104**, was observed in [43, 92]. The key stage of this C–N coupling reaction is probably removal of a hydride ion from the methylene group of the allylamine fragment of the heterocycle. The carbocation **103a**), stabilized in the form of the cycloiminium ion **103b**), is then attacked by the nucleophilic amine with the formation of the imine **104**.



103 **103a** **103b** **104**

R = Ph,  ; Ar = $C_6H_4NO_2$-*p*, C_6H_4Br-*p*, C_6H_4N=NPh

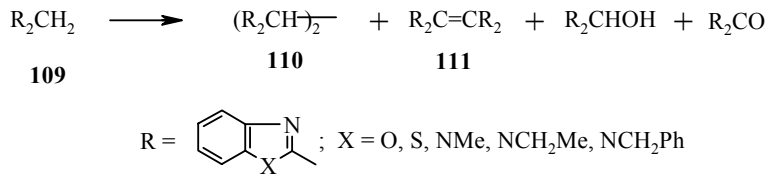
Heterocyclic compounds containing activated CH_2 or CH groups enter into oxidative C–C coupling reactions. 2,4-Disubstituted 5(4H)-thiazolinones **105** were effectively dimerized by the action of potassium permanganate in acetic acid [93]. Here high yields of the symmetrical 4,4'-bithiazolones **106**, the structure of which was confirmed by X-ray crystallographic analysis, were obtained. In certain cases it was possible to isolate the isomeric products from 2,2' and 2,4' cross coupling **107** and **108** respectively, indicating a free-radical mechanism for this reaction.



105 **106** **107** **108**

R^1 = Et, Ph, OEt, SEt; R^2 = Me, CH_2Ph, Ph

Bis(2-benzodiazolyl)methanes and also their oxaaza and thia analogs **109** enter very readily into reaction with potassium permanganate at the methylene group with the formation of compounds having various degrees of oxidation, including C–C coupling products [19]. It was established that the yield of the oxidation products and the ratio depended to a significant degree on the nature of the second heteroatom in the five-membered heterocycle and on the reaction conditions. Since compounds **110** and **111** could also be obtained in the absence of the oxidizing agent [during an attempt to synthesize complexes of the initial **109** with manganese diacetate], the authors indicated the possibility not only of radical but also of carbanionic paths for their oxidation.



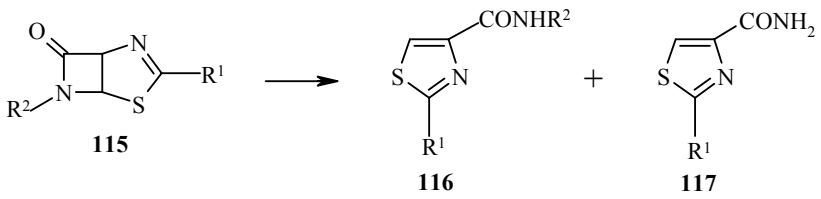
Recently a new oxidative C–C coupling reaction of 4-aryltetrahydropyridines **112** was realized with certain CH acids **113** (acetone, methyl aryl ketones, nitromethane, and dicyanomethane) [60, 61, 94, 95]. Under the influence of potassium permanganate under mild temperature conditions these substrates undergo intermolecular reaction with the formation of 2-methylenetetrahydropyridines **114**. The preferred *E*-configuration of the enamine fragment in compounds **114** (with $R^2 \neq R^3$) was established by X-ray crystallographic analysis and NMR.

R^1 = Me, Et; Ar = Ph, 4-Py, paracyclophan-4-yl;
$R^2 = R^3$ = CN; R^2 = H, R^3 = NO_2, COMe, COPh

6. DECYCLIZATION REACTIONS

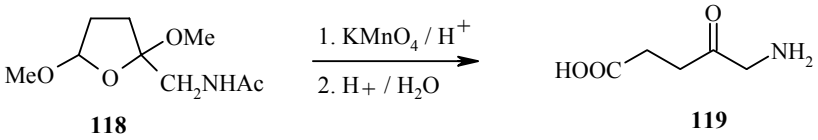
The potassium permanganate anion as a hard oxidizing agent can be used in the decyclization of heterocycles. This makes it possible to synthesize a series of difficultly obtainable compounds with specific arrangements of the substituents and compounds of practical significance.

During the oxidation of compound **115** with potassium permanganate two products **116** and **117** from cleavage of the four-membered lactam ring were isolated [96]. The thiazolidine ring proved more stable on account of its aromaticity.



$R^1 = CH_2OPh$; R^2 = MeOOC–C(Me)$_2$

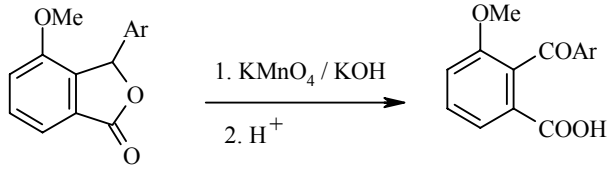
2-Acetamidomethyltetrahydrofuran **118** was oxidized to the aminolevulinic acid **119** with a high yield by potassium permanganate in a dilute aqueous solution of sulfuric acid [97].



118 **119**

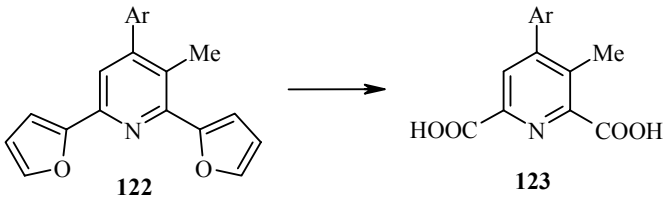
The method was recommended as a convenient method for the synthesis of this selective herbicide and plant growth regulator.

During oxidation with alkaline potassium permanganate at 95°C the phthalide **120** was converted into the disubstituted benzoic acid **121** with a yield of 97% [98].



120 **121**

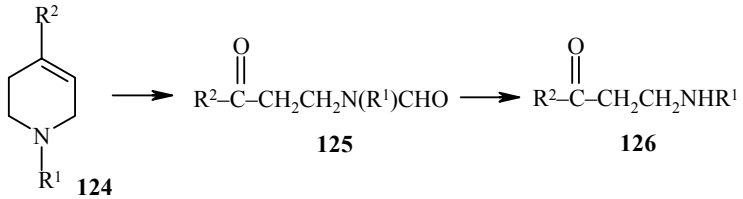
The tetrasubstituted pyridine **122** contains several potential oxidizable substituents. When its solution in acetone or aqueous butanol was heated with potassium permanganate only the furyl radicals were oxidized to carboxyl groups [18 h, yield of acid **123** 70-95%] [99].



122 **123**

Ar = C_6H_4OMe-*p*

The oxidative decyclization of substituted tetrahydropyridines **124** was studied in [43, 100]. It was found that increase in the temperature for oxidation with potassium permanganate (to 50-60°C), the introduction of electron-donating substituents at $C_{(4)}$, the use of phase-transfer catalysis, and quaternization of the substrates resulted in cleavage of the tetrahydropyridines **124** to 1-(formylamino)alkan-3-ones **125** with yields of 43-85%. With increase in the length of the process deformylation of the amides **125**, leading to the amino ketones **126**, became possible.



124 **125** **126**

R^1 = Me, Et, CH_2Ph, $CH_2C_6H_4Cl$-*p*; R^2 = Me, Ph, C_6H_4Me-*p*, C_6H_4OMe-*p*, 4-Py

The sequence of oxidation in the tetrahydropyridines **124** was studied. They are first transformed into 3,4-dihydroxy-2-piperidinones, which then undergo cyclization with the elimination of one carbon atom and the formation of amido ketones [62, 101].

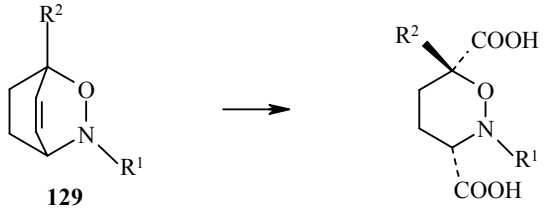
The action of heat on 2,3-dichloroquinoxaline in aqueous potassium permanganate in a neutral medium led to oxidation of the benzene fragment and the formation of dichlorine-substituted pyrazinedicarboxylic acid [102].

An aqueous alkaline solution of potassium permanganate oxidizes 4,7-dihydro-1,3-dioxepins **127** destructively in the cold, giving high yields of the salts of biscarboxymethyl acetals **128** [103].

127 **128**

R = H, Me

During the action of potassium permanganate under the conditions of phase-transfer catalysis oxazabicyclooctene **129** underwent oxidative cleavage at the double bond. As a result a high yield of the racemic tetrahydrooxazine acid **130** was obtained [104].

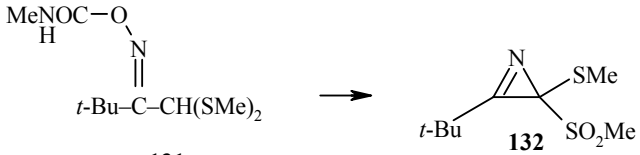


129 **130**

$R^1 = COOCH_2Ph$; $R^2 = CH_2NHCOCH_2Cl$

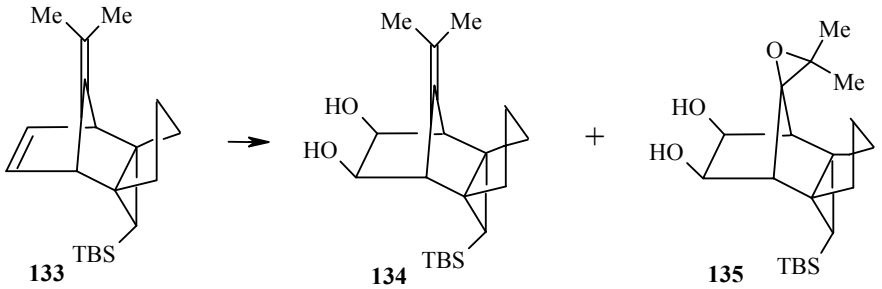
7. CYCLIZATION REACTIONS

Such a strong oxidizing agent as potassium permanganate can be used not only for the cleavage of cyclic bonds but also for the formation of heterocycles. An example of cyclization with the formation of a three-membered nitrogen heterocycle is the oxidation of a water–acetone solution of the oxime derivative **131** with potassium permanganate. The reaction gives a high yield of the substituted 2H-aziridine **132** [105].

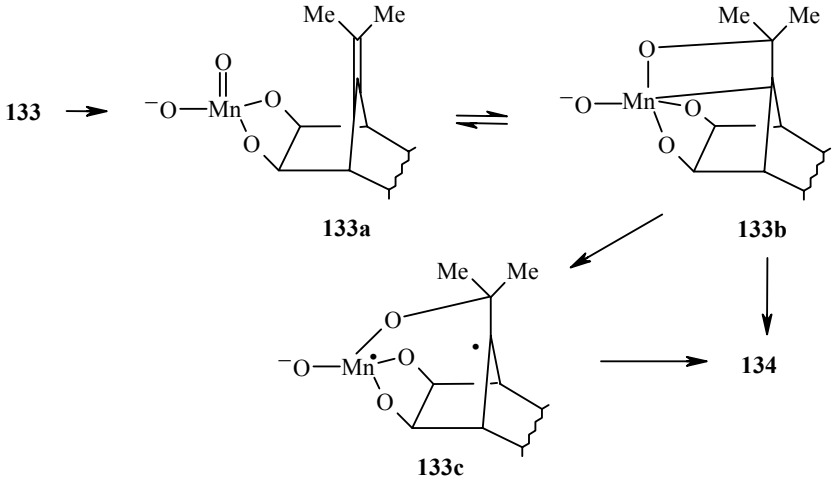


131 **132**

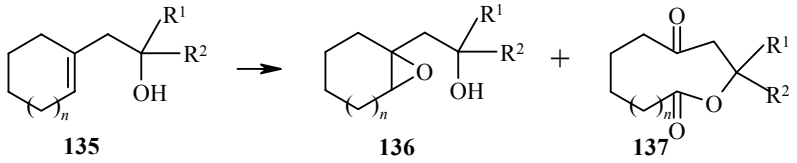
During oxidation of the tricyclic diene **133** with triethylbenzylammonium permanganate at -50°C a mixture of two products was formed – the expected diol **134** (yield 70%) and the oxirane derivative **135** (yield 20%) [106].



The authors attributed the unusual activation of the inert exocyclic double bond to a rare case of epoxidation by the permanganate anion, which in this reaction probably occurred by intramolecular transfer of an oxygen atom in the diester **133a** to its *exo*-double bond through the intermediate products **133b** and/or the radical **133c**.

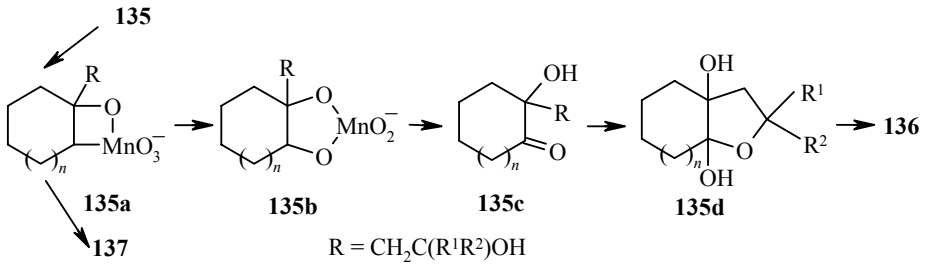


Another case of epoxidation was discovered during oxidation of the homoallyl alcohols **135** in a multiphase heterogeneous system ($KMnO_4$–$CuSO_4$, CH_2Cl_2–*t*-BuOH; 20°C; 3-6 h) [107]. Here the keto lactones **137** were also isolated in addition to the oxiranes **136**.

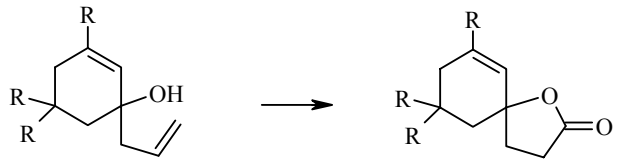


R^1, R^2 = H, Me; *n* = 1–3

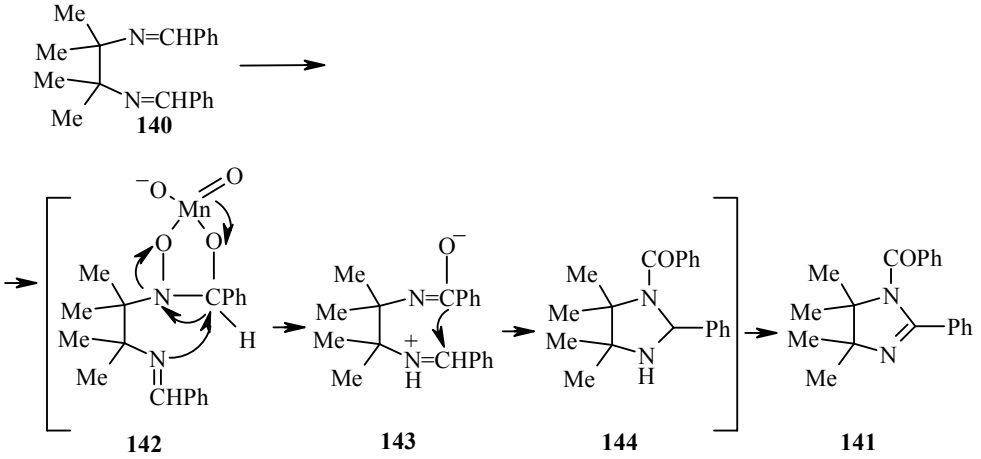
Presumably, the oxiranes are formed directly from the organomanganese compound **135a**, while the ketolactone is preceded by the formation of the diester **135b**, the ketodiol **135c**, and the intramolecular cyclization products **135d**.



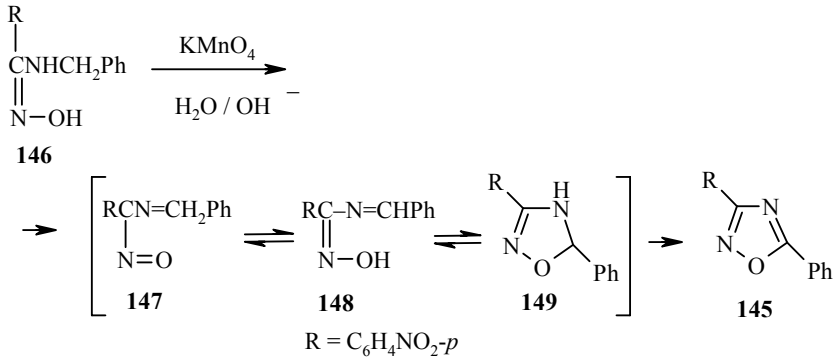
In an analogous system the alcohols **138** undergo oxidative cyclization to the spirosubstituted γ-lactones **139**, which were isolated with yields of 33-62% [108]. In all cases the formation of diols was not observed, which the authors attribute to the chemoselectivity of permanganate deposited on a solid support.



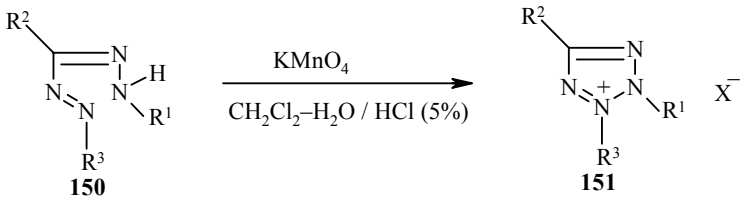
Under the conditions of phase-transfer catalysis the dibenzylidene derivative of 2,3-diamino-2,3-dimethylbutane **140** was oxidized by potassium permanganate (24 h, yield 45%) to the imidazoline **141** [109]. This imidazoline, the structure of which was confirmed by X-ray crystallographic analysis, was probably formed through transformation of the ester **142** into the zwitterion **143**, which underwent cyclization to the imidazolidine **144**. The latter then underwent oxidative dehydrogenation to the stable product **141**.



A new method was proposed for the synthesis of 1,2,4-oxadiazoles **145** by oxidative heterocyclization of the oximes **146** [110]. These oximes are presumably oxidized to the nitrosimines **147**. The latter are tautomers of the imino oximes **148**, which undergo cyclization to the oxadiazolines **149**. During oxidation the latter undergo aromatization to oxadiazoles.



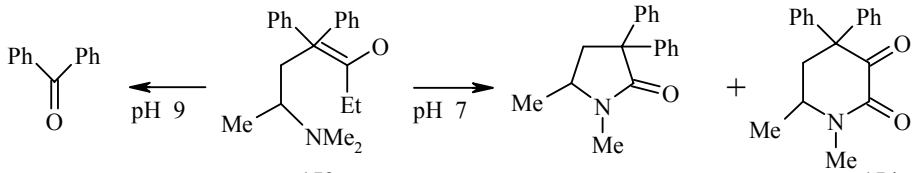
It was shown for the case of a large series of 1,3,5-trisubstituted formazans **150** that potassium permanganate is the best oxidizing agent for their cyclization to 2,3,5-trisubstituted tetrazolium salts **151** [111, 112]. The yield of the salts **151** under the conditions of phase-transfer catalysis amounted to 70-80%. However, addition of the catalyst was evidently superfluous, since its role can be fulfilled by the tetrazolium permanganate formed from the tetrazolium hydroxide as a result of double decomposition. The stability of the salts is increased if the synthesis is conducted in an acidic aqueous medium.



150 **151**

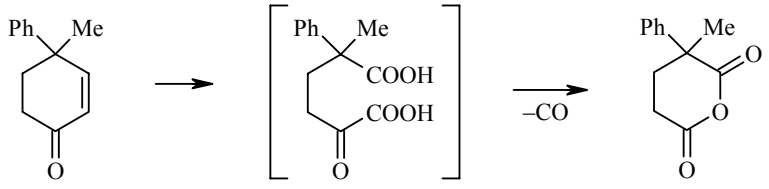
R^1 = Ph; R^2 = Alk, Ar, R^3 = Ar, X = Cl^-, OH^-

A typical example of pH control of the direction of oxidative transformations is the oxidation of methadone **152** by potassium permanganate [113]. In an alkaline medium this tertiary amine undergoes effective degradation to benzophenone. However, oxidation in a neutral medium (in acetone) led to its cyclization with the formation (with high yields) of both five- and six-membered heterocycles – 2-pyrrolidone **153** and 2,3-dioxopiperidine **154** (in a ratio of 4:1).



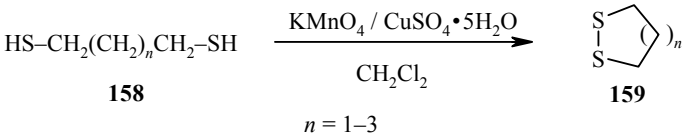
152 **153** **154**

In [114] an original method was demonstrated for transition from the carbocyclic compound **155** to the heterocyclic compound **156** by oxidation of the former with potassium permanganate in acetic anhydride. Initially the α-keto dicarboxylic acid **157** is formed the cyclohexenone **155**, and it is then decarbonylated with subsequent cyclization to the anhydride **156**.

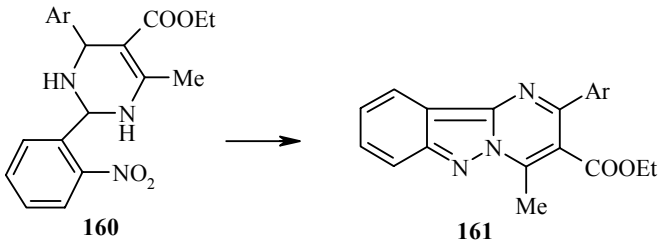


155 **157** **156**

During study of the effect of the heterogeneity of the medium on the direction of oxidation of the 1,2-, 1,4-, and 1,5-dithioalkanes **158** with permanganate it was established that in solution the oxidizing agent leads to the formation of linear sulfonic acids, whereas under heterogeneous conditions (potassium permanganate, deposited on a solid support) these thiols are oxidized to five-, six-, and seven-membered 1,2-dithiocycloalkanes **159** with yields of 45-97% [115].



During the oxidation of the tetrahydropyrimidine **160**, which has an *ortho*-nitrophenyl substituent at $C_{(2)}$, with potassium permanganate intramolecular heterocyclization, resulting in the formation of pyrimido-[1,2-*b*]indazole **161**, was observed [23].



Thus, the examination of recent publications has made it possible to conclude that the potential of such a well known oxidizing agent as the permanganate anion has been far from exhausted. New directions for its use both as a powerful oxidizing agent for the effective introduction of various functional groups and as an agent with oxidizing capability which can even be used for the formation of heterocycles have appeared.

The work was carried out with support from the Russian Fundamental Research Fund (project 99-03-32940a).

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