PREPARATION AND NEW TRANSFORMATIONS OF TRICHLOROMETHYL-SUBSTITUTED ALIPHATIC, AROMATIC, AND HETEROCYCLIC COMPOUNDS* (REVIEW)

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A summary is given for new syntheses of heterocycles starting with trichloromethylarenes and the readily available products of the addition of carbon tetrachloride to functional derivatives of olefins. Applications of the electrophilic trichloromethylation for benzene and thiophene compounds are considered. Information is given on the reactions of trichloromethylarenes with heteronucleophiles, in particular, leading to the synthesis of diaryl-1,2,4- and diaryl-1,3,4-oxadiazoles. The reaction of trichloromethylarenes and pyridines to give the corresponding aromatic aldehydes and N-(4-pyridyl)pyridinium dichloride is discussed.

A current trend in organic synthesis is the use of simple C_1-synthones such as CO, CO_2, and CCl_4 to obtain various functional compounds. In the present review, the author summarizes the recent work in the Laboratory of Heterocyclic Compounds of the Institute of Organic Chemistry of the Russian Academy of Sciences on the synthesis and transformations of trichloromethyl derivatives obtained by the addition of CCl_4 to unsaturated aliphatic compounds and the electrophilic trichloromethylation of aromatic and heteroaromatic systems. Although the transformations of such compounds have been studied for many years, their synthetic potential, primarily in heterocyclic chemistry, has not been exhausted. Known reactions involving heterocyclization with the direct participation of simple compounds such as carbon tetrachloride, chloroform, and chloral were excluded.

NEW SYNTHESES OF HETEROCYCLES FROM ALIPHATIC TRICHLOROMETHYL DERIVATIVES

The readily available products of the addition of CCl_4 to functional derivatives of olefins are convenient starting compounds in the synthesis of various heterocycles. We studied β,β-dichloroacrolein (I), obtained by the addition of CCl_4 to vinyl butyl ether [1], and 3,5,5,5-tetrachloro-2-pentanone (II), which is the product of the addition of CCl_4 to methyl vinyl ketone [2], as such derivatives. Various approaches were attempted for the use of these compounds in the synthesis of heterocycles. Thus, the skeleton of β,β-dichloroacrolein may be fully introduced into the heterocycle formed. A specific example of this approach is found in our new synthesis of 1-aryl-5-chloropyrazoles (III), which were previously difficult to prepare and are valuable intermediates for the preparation of pyrazole derivatives due to their capacity to undergo nucleophilic substitution at $C_{(5)}$ with replacement of the chlorine atom and electrophilic substitution at $C_{(4)}$ [3]. In particular, the N-substituted 1-phenyl-5-chloropyrazolesulfonamides (IV) obtained, as shown in the scheme below, have antiaggregational activity relative to blood [4].

*Dedicated to Professor A. R. Katritzky on the occasion of his sixty-fifth birthday.

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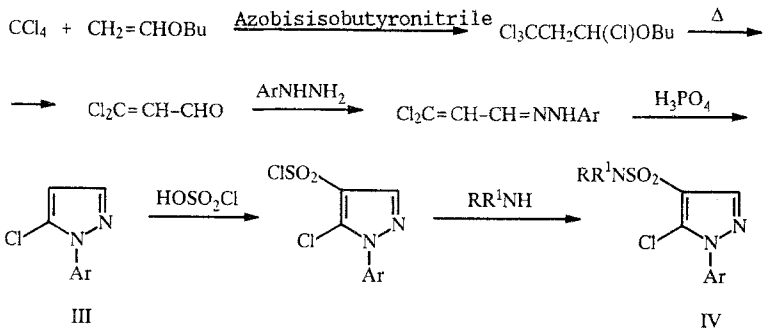
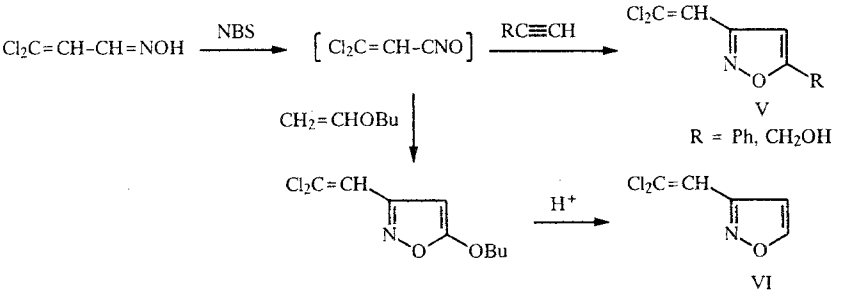
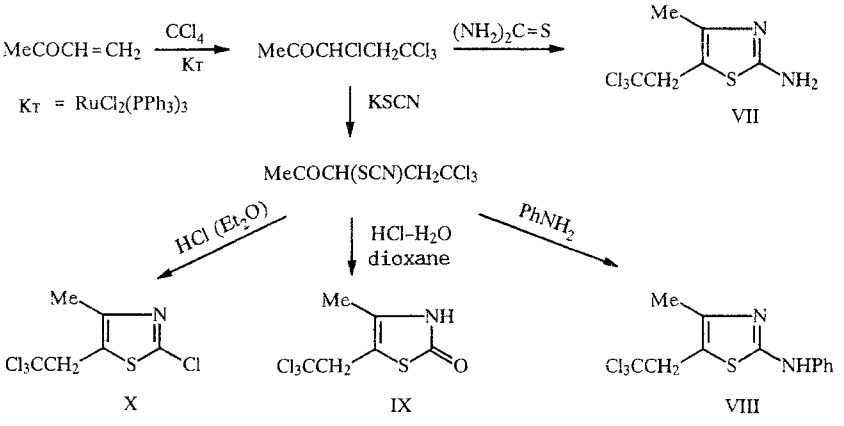


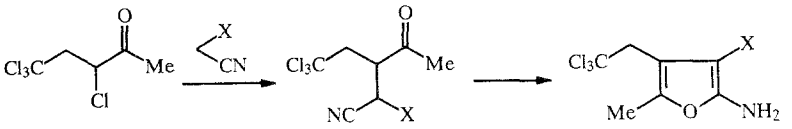
Only the formyl group is used in other syntheses to construct the ring, while the dichlorovinyl group becomes a substituent in the future heterocycle. This has considerable significance for the preparation of physiologically active compounds [5]. For example, the corresponding nitrile oxide was generated from the oxime of β,β-dichloroacrolein. The use of this nitrile oxide in 1,3-dipolar cycloaddition reactions gave a series of substituted isoxazoles V and VI [6].



We also carried out the radical addition of 1,1,1-trichloro-2,2,2-trifluoroethane to vinyl butyl ether and an analogous transformation to give isoxazole derivatives bearing a 3,3,3-trifluoro-2-chloropropenyl substituent [6]. In the case of tetrachloropentanone (II) obtained by the addition of CCl_4 to vinyl methyl ketone, we used reactions with hetero- and C-nucleophiles characteristic for reported syntheses from α-halocarbonyl compounds. A 2,2,2-trichloroethyl group is introduced into the cyclization product and then may be converted into an acetic acid residue or β,β-dichlorovinyl group, which opens interesting possibilities for the preparation of physiologically active compounds. In particular, syntheses were developed for thiazoles VII-X, bearing a 2,2,2-trichloroethyl group at $C_{(5)}$ [7, 8].



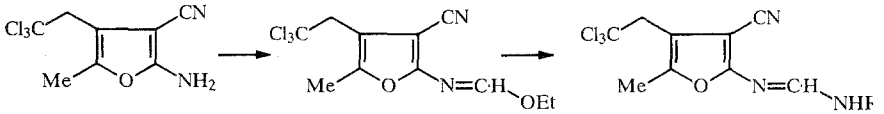
Malonodinitrile and ethyl cyanoacetate were studied as C-nucleophiles. Syntheses were developed for 2-amino-3-cyano- and 2-amino-3-ethoxycarbonyl-5-methyl-4-(2,2,2-trichloroethyl)furanes XI [9, 10].



XI

X = CN, COOEt

2-Amino-3-cyano-5-methyl-4-(2,2,2-trichloroethyl)furane was converted into the corresponding formamidines XII [9, 10], which proved rather stable and could be studied by ^{1}H, ^{13}C, and ^{13}N NMR spectroscopy and x—ray diffraction structural analysis [10].



XII

We should note that such $N_{(1)}$,$N_{(2)}$-disubstituted formamidines ($N_{(1)}$ and $N_{(2)}$ are the sp^2- and sp^3-hybridized nitrogen atoms, respectively) may exist in two tautomeric forms (T_1 and T_2) and both *E* and *Z* isomers are possible for each of these forms. The *Z* isomers may be represented by both synplanar (*sp*) and antiplanar (*ap*) rotamers.

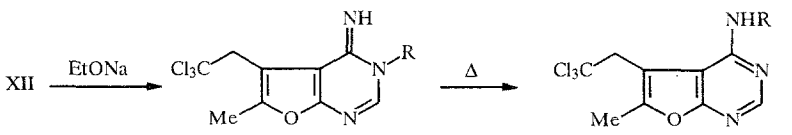
T_1 T_2

Z *sp* Z *ap*

E *sp* E *ap*

Formamidines XII exist in solution as a mixture of two isomers each. As shown in our previous work [10], each of these isomers, independently of the nature of the substituent at the second nitrogen atom, have T_1 structure and are the *E* isomers of $N_{(1)}$-furyl-$N_{(2)}$-R-formamidines. These compounds exist predominantly as antiplanar E_{ap} rotamers.

The cyclization of the amidines by the action of base leads to iminodihydrofuro[2,3-*d*]pyrimidines XIII. These products undergo the Dimroth reaction to give amines XIV, which are derivatives of furo[2,3-*d*]pyrimidine [11].



XIV

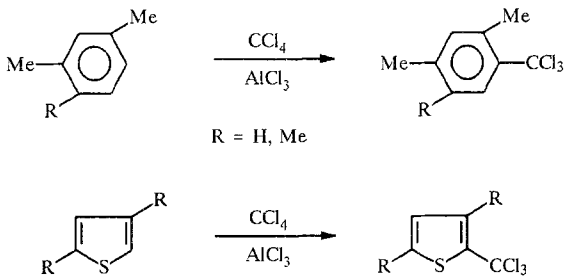
R = H, Alk, Ar. $ArCH_2$, cyclo-Alk

The furo[2,3-*d*]pyrimidine derivatives obtained may be seen as purine base analogs. Various physiological activity should be expected from these compounds and the products of their subsequent transformations. The presence of the 2,2,2-trichloromethyl group in these compounds permits subsequent transformations and the preparation of biologically active 2,2-dichlorovinyl derivatives and derivatives of the corresponding hetarylacetic acids.

ELECTROPHILIC TRICHLOROMETHYLATION OF BENZENE AND THIOPHENE COMPOUNDS

Trichloromethylarenes and trichloromethylhetarenes may serve as valuable precursors in the synthesis of carboxylic acids and their derivatives, symmetrical and asymmetrical diaryl ketones, and various heterocyclic systems. On the other hand, the major method for the preparation of these compounds involves the exhaustive chlorination of methyl substituents of aromatic or heteroaromatic systems. This markedly narrows the possibilities for the preparation of these compounds due to the undesirable chlorination of other substituents or free ring positions. Electrophilic trichloromethylation is an extremely attractive alternative pathway for the preparation of trichloromethylarenes and trichloromethylhetarenes. The activity of carbon tetrachloride as an electrophile is relatively low and its reactions require the use of strong Lewis acids such as aluminum chloride and proceed at close-to-room temperatures. On the other hand, the trichloromethylarenes formed under the reaction conditions are readily converted into active electrophiles, namely, α,α-dichlorobenzyl cations or their heteroaromatic analogs, which exist as $ArCCl_2^+ \cdot MX_n^-$ ion pairs. It is not remarkable that the products of subsequent transformations of these ion pairs such as diaryldichloromethanes or triarylchloromethanes or their diaryl ketone and triarylcarbinol derivatives formed upon hydrolysis rather than the corresponding trichloromethylarenes (trichloromethylbenzene and its derivatives) are the usual products of the reactions of aromatic compounds with carbon tetrachloride [14, 15]. The formation of diaryldichloromethanes and triarylchloromethanes hardly occurs if the CCl_3 group in the trichloromethylarene generated is sterically shielded by two *ortho* substituents as in the case of benzene homologs as mesitylene, durene, isodurene, and pentamethylbenzene [16-18].

In a study of trichloromethyl derivatives aromatic and heteroaromatic compounds, we significantly expanded the scope of electrophilic trichloromethylation and showed that this reaction may be used to obtain compounds having only one shielding substituent in the *ortho* position to the CCl_3 group. Preparative value is found for trichloromethylation of compounds such as *m*-xylene, pseudocumene [19], 2,4-dichlorothiophene [20], and 2,4-di-*tert*-butylthiophene [21, 22] using CCl_4 in the presence of $AlCl_3$.

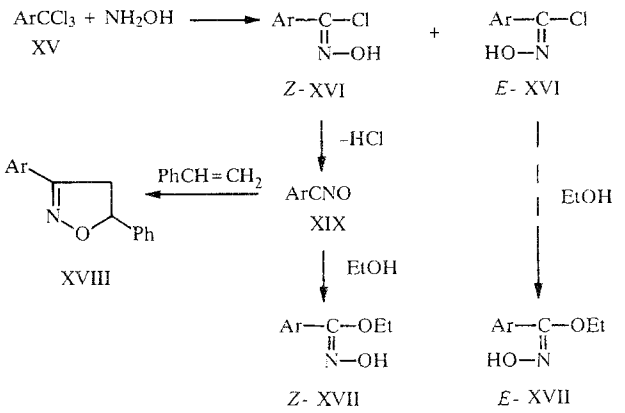


In summarizing our data [19-22], we note that the scope of electrophilic trichloromethylation is more limited for thiophene compounds than for benzene compounds. The greater activity of thiophene compounds and the greater "external" bond angles in the compounds in comparison with benzene compounds presumably facilitate oligomerization under the trichloromethylation conditions and further transformations of its products, leading to dithienylchloromethanes. In particular, while the trichloromethylation of *m*-xylene proceeds rather smoothly [19], its thiophene analog, namely, 2,4-dimethylthiophene as well as other 2,4-dialkylthiophenes with bulkier substituents at $C_{(4)}$ undergo "cross-linking" and oligomerization [22]. This reaction may be achieved only in the case of 2,4-di-*tert*-butylthiophene with very large substituents at both positions, which prevent acid oligomerization but do not completely suppress further transformations of the trichloride product [22]. Since the

reaction of thiophene compounds having electron-withdrawing substituents with carbon tetrachloride requires rather vigorous conditions and leads to "cross-linking" products [23], the 2,4-disubstituted derivatives, in which one substituent is deactivating and the other is activating, and trisubstituted derivatives are promising objects in the study of the electrophilic trichloromethylation of thiophenes.

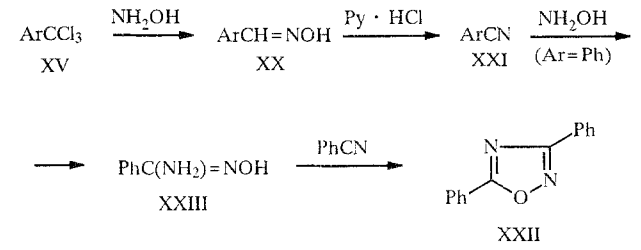
NEW REACTIONS OF TRICHLOROMETHYLARENES WITH HETERONUCLEOPHILES

Trichloromethylarenes are capable of reacting with nucleophiles, usually acting as synthetic equivalents of the corresponding carboxylic acids and giving various reaction products, in particular, heterocyclic derivatives. We have discovered new reactions of trichloromethylbenzene and its derivatives XV as well as trichloromethylthiophenes. One of these reactions involves condensation with hydroxylamine, leading to the formation of hydroxymoyl chlorides XVI [24, 25]. This reaction is carried out in ethanol using equimolar amounts of hydroxylamine hydrochloride and alkali. This process is complicated by alcoholysis, leading to the ethyl esters of the corresponding benzoic acids. Under optimal conditions, specifically, at room temperature, the undesirable reaction pathway can be reduced to a minimum such that ~1:1 mixtures of the corresponding *Z*- and *E*-benzhydroxymoyl chlorides XVIa-XVIc are the major initial reaction products. A mixture of the more sterically hindered *Z*- and *E*-2,4,6-trimethylbenzhydroxymoyl chlorides (XVIc) may be isolated in ~40% yield. The other hydroxymoyl chlorides (XVIa and XVIb) could not be isolated and mixtures of the ethyl esters of *Z*- and *E*-hydroximic acids XVIIa and XVIIb are formed in 60-65% yield. When this reaction is carried out in the presence of styrene, isoxazolines XVIIIa and XVIIIb, which are the products of 1,3-dipolar cycloaddition of the intermediates generated from the *Z*-chlorides [26] of nitrile oxides XIXa-XIXc, are formed in 10-20% yield in addition to ~30% *E*-ethers XVIIa and XVIIb and ~20% *E*-chloride XVIc.

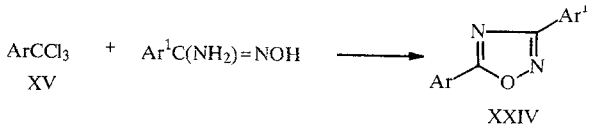


a Ar = 2,4-$Me_2C_6H_3$; b 2,4,5-$Me_3C_6H_2$; c 2,4,6-$Me_3C_6H_2$

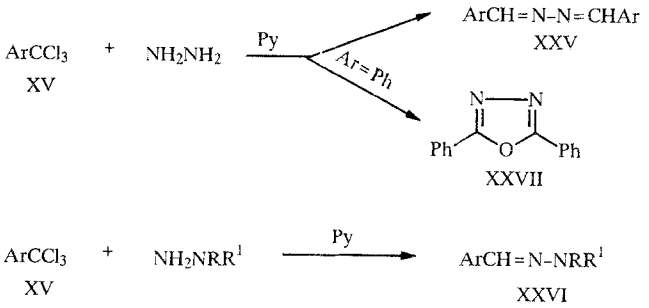
This reaction opens a new pathway for the formation of arenecarbonitrile oxides and is carried out in a single operation by the reaction of trichloromethylarenes with hydroxylamine. However, the preparative use of such an transformation is difficult due to the reaction of the hydroxymoyl chlorides with the solvent (ethanol). In an attempt to avoid such an undesirable side-reaction, we replaced ethanol with pyridine, which should serve both as the solvent and base for the isolation of hydroxylamine from its hydrochloride. The corresponding oximes XX and nitriles XXI were unexpectedly obtained rather than hydroxymoyl chlorides XVI or nitrile oxides XIX. In the case of trichloromethylbenzene, diphenyl-1,2,4-oxadiazole XXII was also formed [27, 28].



The key step in this reaction is the previously unreported reductive oximination of the trichloromethylarenes. Diphenyl-1,2,4-isoxadiazole is probably formed due to the reaction of benzonitrile with hydroxylamine, leading to benzamidoxime XXIII, which reacts with a second benzonitrile molecule and undergoes a heterocyclization reaction previously studied in our laboratory [29, 30]. Alternative pathways such as the dimerization of benzamidoximine and the reaction of benzamidoximine with trichloromethylbenzene were rejected because dimerization requires more vigorous conditions [31], while the reaction of amidoximines with trichloromethylarenes in pyridine proceeds by a different pathway, leading to carboxylic acids from the trichloromethylarenes and nitriles from the amidoximines after work-up of the reaction mixture [32]. At the same time, in the course of a study of reductive oximination, we developed a new, rather general method for the synthesis of 3,5-diaryl-1,2,4-oxadiazoles XXIV from trichloromethylarenes and amidoximines. This reaction is carried out upon heating the components in an inert solvent or in the absence of solvent [32].

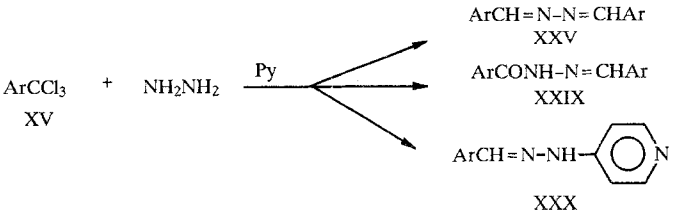


Reductive condensation, which is similar to reductive oximination examined above, also takes place in the reaction of trichloromethylarenes with hydrazines in pyridine and leads to aldazines XXV or hydrazones XXVI. Diphenyl-1,3,4-oxadiazole XXVII is also formed in the reaction of trichloromethylbenzene with hydrazine [28].



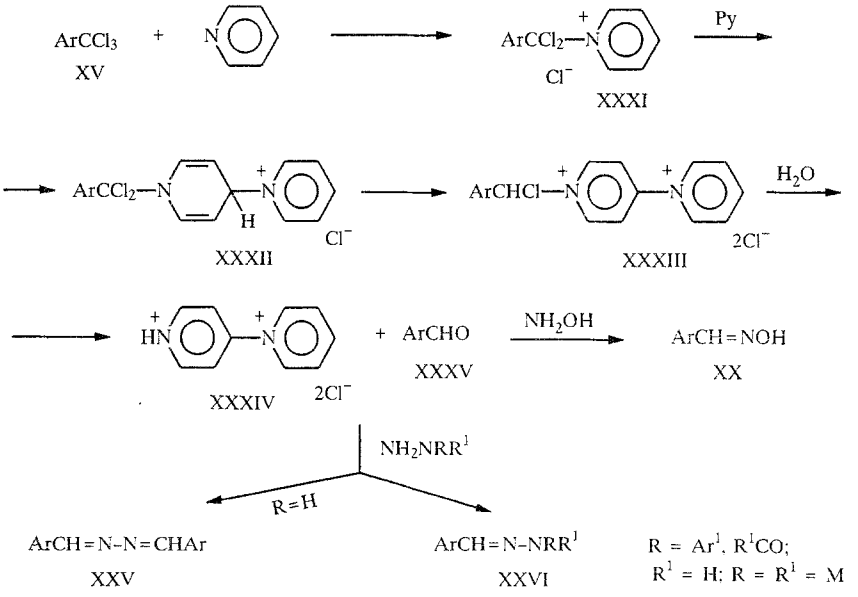
In studying the mechanism for reductive condensation, we assumed that, as in the case of the reaction of hydroxylamine with trichloromethylarenes, hydroxymoyl chloride XVI is formed in the first step, while hydrazinoyl chloride XXVIII is formed from hydrazine and then reduced by hydroxylamine or hydrazine (in our previous work [27, 28], a 5-10-fold excess of the latter compounds was used). A check of this hypothesis did not give unequivocal results [28]. Hydroxylamine and hydrazine, indeed, reduce the corresponding acid chlorides upon heating in pyridine but asymmetrical dimethylhydrazine did not display such capacity.

A study of the effect of the mole ratio of the trichloromethylarenes to hydroxylamine or hydrazine in reductive condensation [33] also did not yield unequivocal results. On one hand, the oxime formation increases, which corresponds to less conversion, with a decrease in the excess of hydroxylamine, while incomplete reduction products XXIX were detected in reactions with hydrazine.



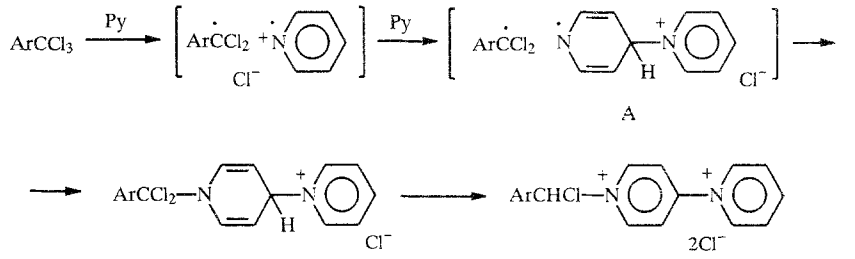
On the other hand, side-reactions were found, primarily the formation of 4-pyridylhydrazones of aromatic aldehydes XXX. Furthermore, a reduction in the amount of hydroxylamine or hydrazine to equimolar relative to the trichloromethylarene remarkably hardly affects the yield of the reductive condensation products XX, XXI, and XXV.

Our subsequent study [34] showed that pyridine is the actual reducing agent in the reductive condensation rather than hydroxylamine or hydrazine. The corresponding pyridinium salt XXXI is formed in the first step of this reaction and may be attacked by a second pyridine molecule with the intermediate formation of a dihydropyridylpyridinium system XXXII. The reduction step proper involves electron transfer to the benzyl carbon atom to give N-(α-chlorobenzylpyridyl)pyridinium salt XXXIII. This salt reacts either directly or as the products of its hydrolysis, N-(4-pyridyl)pyridinium dichloride XXXIV and aromatic aldehyde XXXV, with hydroxylamine or hydrazine to give the corresponding aromatic aldehyde derivatives XX, XXV, and XXVI.



Pyridylhydrazones XXX are probably formed from aldehydes XXXV and 4-pyridylhydrazine arising from hydrazine and pyridylpyridinium salts XXXIII or XXXIV (in this regard, we note that the reaction of dichloride XXXIV with hydrazine is used for the preparative synthesis of 4-pyridylhydrazine [35]).

It is not excluded that the detailed reaction mechanism includes a step involving a one-electron transfer and is reminiscent of the mechanism proposed by Löfas and Ahlberg [36] for the reactions of CCl_4 and CCl_3Br with amidines. Relative to the formation of salt XXXIII, such a mechanism may be given as follows:

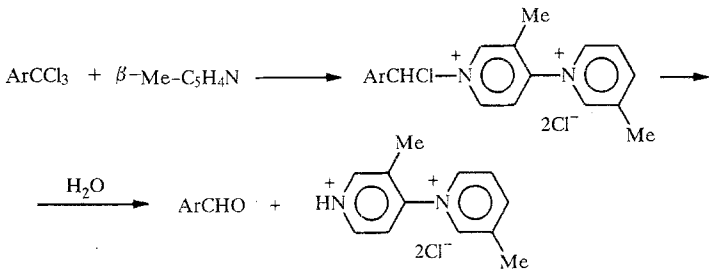


The reduction proper may occur in ion—radical pair A due to the transfer of a hydrogen atom or to the consecutive transfer of a proton and electron [37, 38]. The transfer of a hydrogen atom from the pyridine ring to the benzylic carbon atom is supported by the finding that 2,4,6-trimethylbenzaldehyde deuterated in the formyl group is formed with the reaction is carried out in deuteropyridine [34].

The finding and isolation of the pyridylpyridinium salts described above is, in essence, direct proof for the previously postulated mechanism for the synthesis of N-(4-pyridyl)pyridinium dichloride from pyridine and thionyl chloride, involving initial formation of the corresponding pyridinium salt, its conversion to a dihydropyridylpyridinium salt, and reduction of the sulfinyl sulfur [39-41], i.e., thionyl chloride is reduced during this reaction, while pyridine is oxidized. We also note that many

other syntheses for N-(4-pyridyl)pyridinium dichloride are carried out with the participation of compounds of both forming a salt or complex at the pyridine nitrogen atom and undergo reduction such as SCl_2, PCl_5 [41], and S_2Cl_2 [42] as well as chlorine or bromine (in the presence or absence of a small amount of SO_2Cl_2 or S_2Cl_2 as a "transfer agent") [43, 44].

The abovementioned oxidation—reduction transformations of trichloromethylarenes, which may be seen as new syntheses of aromatic aldehydes and pyridylpyridinium dichloride (a very important intermediate in pyridine chemistry), are rather general and take place also upon the reaction of the trichloromethylarenes with other pyridine bases, in particular, quinoline and β-picoline.



We also cannot exclude that, depending on the structure of the trichloromethylarenes and nitrogen bases, their reaction may proceed by a different pathway as in the Reussert reaction. Clarification of these questions is presently underway.

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