Translated from *Uspekhi Khimii*, **46**, 1698 - 1719 (1977) U.D.C. 547.52 + 547.53 + 547.7 + 547.8

New Data on the Chloromethylation of Aromatic and Heteroaromatic Compounds

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The fundamental methods and applications of the chloromethylation of aromatic and hetero-aromatic compounds as well as ideas concerning the reaction mechanism are considered on the basis of data published mainly during the last ten-fifteen years. The bibliography includes 285 references.

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I. CHLOROMETHYLATION METHODS AND APPLICATIONS OF THE REACTION

Chloromethylation is a specific and most important instance of halogenoalkylation. It consists of the direct substitution of a hydrogen atom by the chloromethyl group. Hydrogen atoms linked not only to carbon but also to heteroatoms may be substituted (see, for example, Refs. 1–5), but chloromethylation at a carbon atom in an aromatic or heteroaromatic ring is of greatest importance, and this in fact will be considered below.

Chloromethylation of aromatic compounds was achieved for the first time in 1898 by Grassi and Maselli[6], who succeeded in obtaining benzyl chloride by the reaction of benzene with trioxymethylene and hydrogen chloride in the presence of zinc chloride. Nowadays chloromethylation is one of the important synthetic methods in organic chemistry.

The studies of the last ten–fifteen years will be mainly considered below, since the fundamental achievements in this field approximately up to 1962 have already been described in a number of reviews[7-9]. As regards the use of chloromethylation methods which have already become classical, we shall as a rule confine ourselves merely to references to the corresponding papers and patents published after 1962. The treatment of studies in which the reaction mechanism is considered as well as certain specific examples of chloromethylation methods which have developed recently will be relatively detailed. These are the chloromethylation of deactivated aromatic and heteroaromatic compounds, particularly the reactions using chloromethyl ethers.

Judging from the data presented in reviews[7-9], the result of the reaction under consideration depends greatly on the nature of the chloromethylating agent, the catalyst, and the process conditions. Effective chloromethylating agents are formaldehyde, paraformaldehyde or trioxymethylene with hydrogen chloride, and monochloromethyl and $\alpha\alpha'$-bischloromethyl ethers. The reaction is carried out in the presence of $ZnCl_2$, $SnCl_4$, $AlCl_3$, BF_3, $FeCl_3$, $TiCl_4$, as well as protic acids—HCl (taken in excess and behaving simultaneously as a reactant), H_2SO_4, H_3PO_4, $ClSO_3H$, and CH_3COOH. Zinc chloride is used most frequently. To increase its activity, it is often used with a small amount of aluminium chloride. However, the employment of $AlCl_3$ as a catalyst can entail the formation of a side product—a diarylmethane derivative—so that aluminium chloride is used mainly for compounds with deactivating substituents for which zinc chloride may be insufficiently effective. The water evolved in chloromethylation in the presence of metal halides hydrolyses the catalyst. In order to remove the water, the chlorides of inorganic acids are sometimes added to the reaction mixture, for example thionyl chloride[10,11]. Chloromethylation may be carried out under both heterogeneous and homogeneous conditions. CH_3COOH, CCl_4, $CHCl_3$, CH_2Cl_2, CS_2, as well as an excess of the chloromethyl ether are widely used as solvents.

The chloromethyl group, which has a mobile chlorine atom, can be converted into a methyl, hydroxymethyl, cyanomethyl, formyl, dialkylaminomethyl, and other functional groups. It is possible to obtain in this way many compounds otherwise difficult to synthesise, particularly biologically active compounds and substances used as intermediates in various syntheses, for example benzene[12-15], biphenyl[16], thiophen[17-24], furan[25], benzofuran[26], isoxazole[27], oxazine[28], benzoxazine[29], benzopyrimidine[30], and xanthotoxin[31] derivatives, as well as chromones[32] and flavones[33,34]. The interaction of bischloromethyl derivatives with various nucleophiles can lead not only to bifunctional compounds but also to complex bicyclic and polycyclic systems (see, for example, Refs. 35–41). Certain chloromethylated aromatic compounds have found industrial applications. Isothiuronium and pyridinium salts of anthraquinone-acridones[42], obtained from chloromethylderivatives, are used as dyes. Technical syntheses of pyromellitic dianhydride, trimellitic anhydride[43], terephthalic acid[44], phthalic and benzenepolycarboxylic acids[45], surfactants[46], etc. have been developed on the basis of mono- and bis-chloromethyl derivatives of aromatic hydrocarbons. The use of the chloromethylation reaction in the manufacture of ion-exchange resins has assumed significant importance recently[47-49].

II. CHLOROMETHYLATION BY TREATMENT WITH FORMALDEHYDE AND HYDROGEN CHLORIDE

Chloromethylation is usually carried out with the aid of formaldehyde (normally in the form of formalin or paraformaldehyde) and hydrogen chloride in aqueous or non-aqueous media. Chloromethylation with formaldehyde in HCl was extensively redeveloped at one time by Blanc[50],

which led to his name being given to this reaction [7,51], although the process conditions do not differ from those described by Grassi and Maselli [6]. Zinc chloride is usually employed as the catalyst [52-58], more rarely tin(IV) chloride [59] or aluminium chloride [57]. However, when the CH_2Cl group is introduced into aromatic compounds containing activating substituents, hydrogen chloride may serve as the catalyst [44,60-69]; in certain cases the reaction is carried out under pressure [43]. Other protic acids are also used successfully as catalysts—sulphuric [70], phosphoric [56,57], and perchloric [58]. The chloromethylation method considered here is applicable also to the compounds containing simultaneously activating and deactivating substituents, for example to hydroxybenzoate esters [71-74] and dimethoxybenzaldehydes [75]. Studies on the chloromethylation of the benzene rings of the condensed and partly hydrogenated 2-benzofuranone and 3,4-dihydrocoumarin [76,77] as well as phenoxathiin [78] systems are related to the above investigations. The reactions of pyromucic acid esters [79], 2,5-dimethylthiophen [80], 2-phenylbenzofuran [81], 1,2,5-thiadiazole [82], substituted α-pyridone [83], and a derivative of tetrahydrocorrin [84] may be quoted as examples of the chloromethylation of heterocycles by treatment with formaldehyde and HCl.

The chloromethylation of deactivated aromatic compounds by treatment with formaldehyde and HCl is frequently carried out in concentrated sulphuric acid [85-88]. In some cases, the reaction is performed in the absence of HCl; the chloromethylating mixture is then prepared from paraformaldehyde, chlorosulphonic acid, and concentrated sulphuric acid [89,90].

Specific difficulties arise in the chloromethylation of alkyl aryl ketones. In the absence of activating substituents in the benzene ring, as in the case of dialkyl ketones (see, for example Dermer and Newcombe [91]), the α-position in the side chain is substituted. For example the chloromethylation of acetophenone in the side chain is carried out by treatment with paraformaldehyde and HCl in glacial acetic acid at 100°C in the presence of phosphoric or sulphuric acid [92-95]. The use of paraformaldehyde and concentrated hydrochloric acid in acetic acid, in the presence of 70% $HClO_4$, makes it possible to introduce two CH_2Cl groups into the methyl group of acetophenone [96].

It is quite likely that chloromethylation of the side chain proceeds via the mechanism of the Prins reaction [97-99]—the condensation of formaldehyde with olefins in the presence of acid catalysts. As a result of the interaction of formaldehyde with the catalyst, the hydroxymethyl cation is produced in this reaction and then attacks the double bond of the olefin. The chloromethyl derivative may be formed in the presence of HCl—for example, on treatment with paraformaldehyde and HCl in acetic acid, 1,1-diphenylethylene is converted into 3-chloro-1,1-diphenylprop-1-ene [100].

We believe that, in the reaction involving alkyl aryl ketones, the $(CH_2OH)^+$ cation attacks the enolic form of the ketone, after which the newly formed cation is stabilised by the elimination of a proton, this being followed by the substitution of the hydroxy-group by chlorine. This process may be represented schematically as follows:

$$CH_2O + HX \rightleftarrows HO\overset{+}{C}H_2 + X^- ,$$

$$RC(=O)-CH_3 \rightleftarrows R-C(OH)=CH_2 ,$$

$$R-C(OH)=CH_2 + \overset{+}{C}H_2OH \rightarrow R-\overset{+}{C}(OH)-CH_2CH_2OH ,$$

$$R-\overset{+}{C}(OH)-CH_2CH_2OH \xrightarrow{-H^+} R-C(OH)=CHCH_2OH ,$$

$$R-C(OH)=CHCH_2OH + HCl \rightarrow R-C(=O)-CH_2CH_2Cl .$$

It is important to note that the introduction of electron-donating substituents into the benzene ring of an alkyl aryl ketone alters the mode of chloromethylation—the CH_2Cl group enters the aromatic ring and not the side chain [92,101-106]. It therefore becomes understandable why acyl derivatives of activated heteroaromatic systems (furan [107], thiophen [108-114], and selenophen [115]) are also chloromethylated in the ring.

Chloromethylation is a typical electrophilic substitution reaction. Nazarov and Semenovskii [116] have shown that the amount of the *meta*-chloromethyl derivative increases in the following sequence in chloromethylation, as in other electrophilic substitution reactions (nitration and halogenation):

$$C_6H_5CH_3 < C_6H_5CH_2COOC_2H_5 < C_6H_5CH_2Cl .$$

In the chloromethylation of halogenobenzenes, a gradual increase of the amount of *o*-isomers is observed on passing from fluorobenzene to iodobenzene [116]. A similar variation of the proportions of the isomers occurs, for example, in the nitration of halogenobenzenes [117]. The study of the proportions of the isomers obtained in the chloromethylation of alkylbenzenes [116,118,119] has shown that they fully obey the rules established for other electrophilic substitution reactions. The chloromethyl group enters mainly the *para*- and *ortho*-positions. Substitution in the *meta*-position is observed to only a slight extent and the fraction of the *meta*-isomer increases for alkylbenzenes with increase in the bulk of the alkyl group in the sequence $CH_3 < C_2H_5 <$ iso-$C_3H_7 <$ t-C_4H_9. For example, the chloromethylation of toluene results in the formation of only traces of the *meta*-chloromethyl derivative, while t-butylbenzene gives rise to 6.1% of *meta*-t-butylbenzyl chloride [119].

Comparison of the results of the chloromethylation [116,120] of toluene, ethylbenzene, cumene, and other hydrocarbons differing in the bulk of the alkyl substituent established that the amount of *o*-isomer decreases from 51.7% to 0% in the series of C_6H_5Alk derivatives, where Alk = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, iso-C_4H_9, cyclo-C_6H_{11}, iso-C_3H_7, or t-C_4H_9†. This phenomenon is due to the increasing steric hindrance in the *o*-position on passing from toluene to t-butylbenzene. The same type of regular decrease of the amount of *o*-isomer is characteristic of other electrophilic substitution reactions [121].

It is noteworthy that the available quantitative literature data for the relative rates of chloromethylation of aromatic hydrocarbons are extremely contradictory at first sight. Thus the observed ratio of the rates of chloromethylation of toluene and benzene (k_t/k_b) varies within very wide limits—from 3 [122,123] to 30 [124] and even to 112. [125] Incidentally, one should note that in the above studies [122-125] the reactions were carried out under different conditions and different chloromethylating agents were used. Furthermore, we believe that some of the workers [122,123] employed an inadequate analytical method and it is quite likely that errors might have been made in the determination of the concentration of chloride ions.

† Traces of *o*-t-butylbenzyl chloride have been detected [119].

Vavon et al.[122] used for chloromethylation a monochloromethyl ether in glacial acetic acid at 100°C and measured the rate of reaction on the basis of the amount of HCl evolved on hydrolysis of the ether which failed to react. Szmant and Dudek[123] carried out the reaction by treatment with paraformaldehyde and HCl in glacial acetic acid at 85°C. The kinetics were followed from the change in the concentration of chloride ions during the reaction. Brown and Nelson[125] were unable to reproduce the results of Vavon et al.[122] and Szmant and Dudek[123] and carried out the reaction under other conditions, namely they used trioxymethylene and gaseous HCl in the presence of zinc chloride as the catalyst in solution in glacial acetic acid at 60°C. The ratio k_t/k_b was found by the method of competition kinetics, by a quantitative determination of the corresponding hydrocarbons, isolated after the reduction of the chloromethyl derivatives with lithium tetrahydroaluminate‡. For the chloromethylation rate constant ratio $k_t/k_b = 112$ obtained by Brown and Nelson[125], a linear relation is observed between the logarithms of the partial rate factors for substitution in the *p*-position ($\lg f_p$) and the selectivity factors $F_S = \lg(f_p/f_m)$, where f_m is the partial rate factor for substitution in the *m*-position, as for other electrophilic substitution reactions.

The fact that chloromethylation is an electrophilic substitution reaction is consistent also with the reaction constant ρ, which has been determined[124,126] and found to be of the order of −5. In the above studies, paraformaldehyde with hydrochloric acids were used as the chloromethylating agent. The reaction mixture was analysed for hydrochloric acid and formaldehyde at specified time intervals. The isomeric composition of the chloromethylated derivatives was determined after their catalytic reduction to the corresponding polymethylbenzenes. The experimental relative rates agree satisfactorily with data calculated by Condon's method[127] from the partial rate factors for substitution in the *o*-, *m*-, and *p*-positions in toluene.

Attempts to elucidate the mechanism of chloromethylation by treatment with formaldehyde and HCl have been made frequently. Darzens[128] believed that chloromethyl acetate $ClCH_2OOCCH_3$ is the chloromethylating agent when the reaction is carried out in acetic acid:

$$CH_2O + CH_3COOH + HCl \rightarrow ClCH_2OOCCH_3 + H_2O\,,$$
$$ArH + ClCH_2OOCCH_3 \rightarrow ArCH_2Cl + CH_3COOH\,.$$

However, Brown and Nelson[125] showed that the reaction of benzene with this ester at 75–80°C for 16 h without catalysts and for 4 h in the presence of zinc chloride does not give rise to benzyl chloride. Chloromethyl acetate can be used for the chloromethylation of benzene if the mixture is allowed to stand for 100 h.

The reaction of CH_2O and HCl may lead to the formation of CH_2Cl_2, but the latter is not a chloromethylating agent: the attempt to chloromethylate benzene by methylene chloride in the presence of zinc chloride was unsuccessful[129]. It was believed[130] that the chloromethylating agent is $\alpha\alpha'$-bischloromethyl ether formed in the reaction between CH_2O and HCl. In fact, as will be shown in the next section, the formation of the bischloromethyl ether is most likely in the chloromethylation of relatively inactive compounds under severe conditions. On the other hand, in chloromethylation under mild conditions, particularly in aqueous solutions, other possibilities must be considered.

Together with the mechanism presented above, two ionic mechanisms have also been put forward for the chloromethylation reaction. The first[131] presupposes that the attacking species is $[CH_2Cl]^+$, which may be formed in the first stage in conformity with the following reaction scheme:

$$CH_2O + HCl + H^+ \overset{K_1}{\rightleftarrows} CH_2OHCl + H^+ \overset{K_2}{\rightleftarrows} \overset{+}{C}H_2Cl + H_2O\,,$$
$$ArH + \overset{+}{C}H_2Cl \overset{k}{\rightarrow} ArCH_2Cl + H^+\,.$$

According to this scheme, the rate of reaction should be described by the equation

$$\frac{dx}{dt} = k\,[ArH][\overset{+}{C}H_2Cl] = kK_1K_2\frac{[ArH][CH_2O][HCl][H^+]}{[H_2O]}\,,$$

where K_1 and K_2 are the equilibrium constants and k is the rate constant.

However, the above mechanism conflicts with experimental data[132]: when the reaction is carried out in H_2SO_4 in the absence or presence of chloride ion (LiCl), the rate constant is virtually the same, i.e. the chloride ion does not affect the rate and yet if the reaction involves the mechanism under consideration such an effect should have been observed, because the rate equation includes the concentration of HCl. On the basis of this mechanism, the rate of the chloromethylation reaction should be described by the equation for third-order kinetics, which also conflicts with experimental data[133].

Another mechanism which postulates the formation of the hydroxymethyl cation $[CH_2OH]^+$ and subsequent attack by the latter on the aromatic compound appears to be most justified at the present time; in the next stage, the hydroxy-group is substituted by a chlorine atom, which leads to the formation of the final compound[132,134,135]. The conclusion that the attacking species is the hydroxymethyl cation was reached[124] particularly on the basis of the finding that the formation of *o*- and *p*-isomers in identical proportions is observed in the bromomethylation and chloromethylation of toluene, ethylbenzene, and cumene. This shows that in both cases the same attacking species is active, consisting of the protonated form of formaldehyde, namely $[CH_2OH]^+$§. If the reaction involved the halogenomethyl ion, then bromomethylation should have produced a greater amount of the *p*-isomer than chloromethylation, since the bulk of the bromomethyl group is significantly greater than that of the chloromethyl group. Furthermore, it has been shown[134] that, under the chloromethylation conditions, the hydroxy-group in the benzyl alcohol is fully substituted by chlorine.

This conclusion has been confirmed by the kinetic studies of Ogata and Okano[132] on the chloromethylation of mesitylene by treatment with formaldehyde and HCl in 90% aqueous acetic acid and by Farberov and coworkers[135] on the chloromethylation of xylenes and pseudocumene by

‡ According to recently published data[284], the analytical method employed by Brown and Nelson[125] leads to an unduly high value of k_t/k_b. It is possible to infer from the results obtained by gas–liquid chromatography directly for mixtures of the chloromethyl derivatives formed under the conditions of competing reactions[284] that this quantity is about 30 (cf. Mironov et al.[124]).

§ In this connection, it is interesting to note that at equilibrium in acid media (pH < 2.6) formaldehyde is present in the form of the hydroxymethyl cation[136].

treatment with formaldehyde and hydrochloric acid. The following chloromethylation mechanism was proposed[135]:

$$CH_2O + H^+ \underset{K}{\overset{\text{fast}}{\rightleftharpoons}} \overset{+}{C}H_2OH ,$$

$$ArH + \overset{+}{C}H_2OH \xrightarrow{\text{slow}} [\overset{+}{Ar}HCH_2OH] ,$$

$$[\overset{+}{Ar}HCH_2OH] \rightarrow ArCH_2OH + H^+ ,$$

$$ArCH_2OH + HCl \xrightarrow{\text{fast}} ArCH_2Cl + H_2O .$$

If it is postulated that the rate-limiting stage is the addition of the protonated form of formaldehyde to the molecule of the aromatic hydrocarbon, then kinetic analysis leads to the following expression for the rate of reaction:

$$\frac{dx}{dt} = k[ArH][\overset{+}{C}H_2OH] = kK[ArH][CH_2O][H^+] = K_F[ArH][CH_2O] ,$$

where k is the rate constant, K the equilibrium constant, and $K_F = kK[H]^+$.

After taking logarithms in this equation, we obtain the relation

$$\lg K_F = -H_0 + \text{const} ,$$

where H_0 is the Hammett acidity function.

Experimental data confirm the proposed mechanism, since it has been observed that the rate of reaction is directly proportional to the product $[ArH][CH_2O]$. A linear relation has been obtained[135] between the logarithm of the rate constant and the Hammett acidity function for the monochloromethylation of *m*-xylene and pseudocumene by treatment with formaldehyde and hydrochloric acid. The concentration of hydrochloric acid and the molar ratios of hydrochloric acid, the hydrocarbon, and formaldehyde have a considerable influence on the rate of chloromethylation, which confirms the acid-catalysed reaction mechanism.

Detailed studies have shown that the monochloromethylation of *m*-xylene and pseudocumene by treatment with $(CH_2O)_n$ and HCl for a constant acidity function H_0 is described by a second-order kinetic equation, which confirms the last mechanism[135]. When the reaction was carried out in different solvents—formic, acetic, and propionic, and butyric acids and dioxan—it was observed that the rate of chloromethylation in the presence of aliphatic acids is much higher than in dioxan and water[137]. According to the authors, this phenomenon can be accounted for by the formation of the protonated form of the aliphatic acid, which exhibits a high proton-donating capacity. This results in an increase of the concentration of $[CH_2OH]^+$ and of the rate of the rate-limiting stage of reaction (2). If the reaction is performed in acetic acid in the presence of zinc chloride, the latter forms with acetic acid the complex acid $H_2[ZnCl_2(OCOCH_3)_2]$, which is just as strong as inorganic acids[138]. The acceleration of the process can be explained by the increase of acidity of the medium, leading to an increase of the concentration of $[CH_2OH]^+$ ions[139].

The mechanism of chloromethylation by treatment with CH_2O and HCl in the presence of zinc chloride in the absence of a catalyst can be represented as follows[8]:

$$CH_2O + HCl + ZnCl_2 \rightleftharpoons [CH_2OH]^+ ZnCl_3^- ,$$

$$ArH + [CH_2OH]^+ ZnCl_3^- \rightleftharpoons \text{(arenium ion, R, H, } CH_2OH\text{)} \quad ZnCl_3^- \xrightarrow{HCl} ArCH_2Cl + ZnCl_2 + H_2O ,$$

or

$$\overset{\delta+}{CH_2O} \rightarrow \overset{\delta-}{ZnCl_2} + \text{(benzene)} \rightleftharpoons Cl_2Zn{-}O{-}C(H)(H)\text{-(arenium ion)} \xrightarrow[-H^+]{HCl} \text{(benzene)}{-}CH_2Cl + H_2O + ZnCl_2 .$$

Together with the formation of monochloromethyl derivatives, bischloromethyl derivatives are produced as an admixture. By carrying out the reaction with a specific reactant ratio, it is possible to drive it towards the formation of bischloromethyl derivatives. For example, the bischloromethylation of xylene and pseudocumene[135] at 95° requires a considerable excess of hydrochloric acid, (8–10 moles) and paraformaldehyde (4–6 moles) relative to the stoichiometric amount. Very few studies have been made on the kinetics and mechanism of the formation of bischloromethyl derivatives. According to Ishii and Yamashita[140], the chloromethylation of monochloromethylxylene is not described by the equation for zero-order kinetics. However, on the basis of a study of the kinetics of the formation of the products of the bischloromethylation of *m*- and *p*-xylenes, Mironov et al.[141] proposed for this reaction the same mechanism as for monochloromethylation; the observed kinetic relations were interpreted in terms of the second-order equation for acid-catalysed reactions.

The most important side reaction in the chloromethylation process is the formation of diarylmethanes as a result of the further condensation of the initial compounds and the chloromethyl derivative obtained. It has been reported that the formation of diarylmethane may be inhibited by employing arsenic(III) chloride or arsenic(III) oxide as the catalyst[142]. In some cases, this reaction may be of independent interest, since it gives rise to polymethylbenzenes (as a result of the hydrocracking of the corresponding diarylmethanes[143]), benzophenonepolycarboxylic acid, and their anhydrides[144]. It has been shown by studying the kinetics of the chloromethylation of pseudocumene and *m*-xylene and the subsequent synthesis of diarylmethanes in the presence of toluene-*p*-sulphonic acid that the condensation reaction is described by the equation for second-order kinetics[133] (first order with respect to CH_2O and first order with respect to HCl). The slowest stage, determining the overall rate of reaction, is the addition of the hydroxymethyl cation to the aromatic hydrocarbon molecule, as in chloromethylation[133].

It has been suggested recently[145] that the active chloromethylating species is the protonated form of the hypothetical chloromethanol ($ClCH_2\overset{+}{O}H_2$). The overall mechanism may be represented by a scheme[145] similar to that proposed previously[146]:

$$CH_2O + 2HCl + ZnCl_2 \leftrightharpoons ClCH_2\overset{+}{O}H_2ZnCl_3^- ,$$

$$H_2\overset{+}{O}CH_2Cl + \text{(benzene, R)} \rightleftharpoons \text{(arenium ion, R, } ClH_2C, H\text{)} \xrightarrow{-H^+} \text{(benzene, R, } CH_2Cl\text{)} .$$

This mechanism does not conflict with the kinetic data discussed above (first order with respect to CH_2O and ArH), but it gives rise to a number of objections. In the first place, the authors who proposed it[145] established themselves that the $ClCH_2\overset{+}{O}H_2$ species exists only below −65 °C even in a very acid medium. Chloromethylation is possible in principle at such temperatures (see, for example, Ref. 147), but the reaction is usually carried out at a higher temperature. On the other hand, the above mechanism presupposes the direct introduction of the CH_2Cl group, and not CH_2OH, into the aromatic ring. A number of arguments against this view were examined above. Furthermore, there is direct experimental evidence in support of the primary formation of hydroxymethyl derivatives, which are converted into chloromethylation products only in later stages[106,148].

III. CHLOROMETHYLATION BY TREATMENT WITH CHLOROMETHYL ETHERS

1. Conditions and Characteristic Features of the Use of the Reaction

Another important group of chloromethylating agents are chloromethyl ethers, mainly monochloromethyl (MCME) and $\alpha\alpha'$-bischloromethyl (BCME) ethers. Chloromethylation by alkyl chloromethyl ethers was described for the first time by Sommelet[149]. By treating benzene with α-monohalogenoalkyl ethers in the presence of $AlCl_3$ in CS_2, he obtained a mixture of the benzyl ether and benzyl chloride. He believed[149] that the primary product is an ether which is readily converted into the chloromethyl derivatives under the influence of the HCl liberated during the reaction:

$$ArH + ClCH_2OR \xrightarrow[CS_2]{AlCl_3} ArCH_2OR,$$
$$ArCH_2OR \xrightarrow{HCl} ArCH_2Cl.$$

Apart from $AlCl_3$, the catalysts used for this reaction were $ZnCl_2$, $SbCl_5$, and $SnCl_4$; the author believed that $SnCl_4$ was the most suitable catalyst. Aluminium chloride usually gives rise to further condensation reactions with formation of diphenylmethane and high-molecular-weight products.

Vavon and Bolle[150] suggested that aromatic hydrocarbons be chloromethylated under homogeneous conditions, namely by treatment with MCME in acetic acid without a catalyst. However, under these conditions the reaction is much slower than in the presence of a catalyst. Presumably, on treatment with MCME in acetic acid, chloromethylation may be accompanied by acetoxymethylation, since solutions of MCME in acetic acid contain methoxymethyl acetate[151]. However, the product of the acetoxymethylation of mesitylene was not isolated. As stated above, the substituted benzyl acetate formed is readily cleaved by the HCl evolved or MCME.[151] Lock[129] showed that the optimum conditions for chloromethylation by treatment with MCME are the use of zinc chloride as the catalyst in a heterogeneous medium with an excess of the aromatic compound as the solvent.

The chloromethylation with $\alpha\alpha'$-bischloromethyl ether was also carried out for the first time in the synthesis of benzyl chloride and related compounds[130]. The chloromethylating agent was the unpurified product obtained by treating paraformaldehyde or an aqueous formaldehyde solution with hydrogen chloride; Tishchenko[152] showed that it contains mainly BCME¶. A certain amount of MCME is also present in this mixture, because formaldehyde usually contains an admixture of methanol[156,157] and the interaction of CH_3OH, CH_2O, and HCl is known to be a preparative method for synthesising MCME.[158–160]

It has been shown[161] that the mixture obtained when HCl is passed into formalin contains, apart from MCME, and BCME, the bischloromethyl acetal of formaldehyde $CH_3(OCH_2Cl)_2$, which can also serve as a chloromethylating agent. This conclusion was reached in a study of the chloromethylation of selenophen and its homologues. It is of interest to note that, according to Yur'ev et al.[161] treatment in acetic acid with BCME, specially prepared and purified by a standard method[162], failed to yield chloromethylselophens. We believe that this finding can be explained by the fact that the reaction mixture does not contain HCl, which usually plays the role of the catalyst. Furthermore, BCME obtained by the standard method[162] contains paraformaldehyde and, according to Pesin and D'yachenko[163], bases and pseudobases (urotropine, dimethylformamide and paraformaldehyde) inhibit chloromethylation with BCME. It must be emphasised that the mixture of MCME and BCME usually used for chloromethylation always contains an admixture of HCl, since it is obtained by passing HCl into formalin and is used in the reaction without preliminary purification.

The data presented permit the conclusion that the chloromethylation by treatment with CH_2O and HCl may result in the formation of BCME and MCME. It may be that, in the chloromethylation of comparatively reactive aromatic compounds in an aqueous medium, the rate of formation of the ethers is low. On the other hand, the chloromethylation of deactivated aromatic compounds with paraformaldehyde and hydrogen chloride in the presence of H_2SO_4, oleum, or HSO_3Cl actually proceeds under conditions in which BCME is formed on a preparative scale[162]. The chloromethylation of deactivated aromatic compounds takes place fairly slowly and the rate of reaction may therefore be comparable to the rate of formation of BCME in the reaction medium. Evidently, under such conditions the reaction mechanism must reflect the involvement of the chloromethyl ethers. The problem of the mechanism of chloromethylation by BCME and MCME is discussed below. Examples of the employment of chloromethyl ethers for the synthesis of the corresponding substituted aromatic and heteroaromatic derivatives are also given.

Chloromethyl ethers are used as chloromethylating agents for a wide variety of compounds differing greatly in their reactivities. The reactivity of BCME is higher than that of MCME;[130] furthermore, it depends significantly on the catalysts employed and also on different impurities and additives. The chloromethylation of reactive aromatic compounds (hydrocarbons with *ortho–para* directing substituents and heterocycles) is usually carried out by treatment with MCME in acetic acid[164–166] or in carbon disulphide in the presence of tin(IV) chloride at 0°C.[167,168] Compounds containing simultaneously activating and deactivating substituents, for example nitrophenols, are chloromethylated by treatment with MCME or BCME when heated in the presence of catalysts—usually zinc chloride[169,170]. Under the same conditions, it is possible to chloromethylate also fairly stable aromatic compounds[171]. Deactivated compounds are normally acted upon by chloromethyl ethers in sulphuric acid or oleum, sometimes in the presence of chlorosulphonic acid[172–174].

Chloromethylation with chloromethyl ethers has come to be widely used in the manufacture of ion-exchange resins. Polystyrene[175–183]†, the copolymers of styrene with divinylbenzene[185–193], *NN'*-arylenedimethacrylamides[194,195], 9-alkyl-3-vinylcarbazoles[196], divinylbenzene, acrylonitrile[48], and ethylene terephthalate[197], polyphenylisoprene[198], poly-(*p*-phenylene-ethylene)[199], and other polymers have been chloromethylated for this purpose. The chloromethyl group usually enters the *p*-position and to a small extent the *o*-position in the aromatic ring. The reaction is frequently accompanied by side processes—the polymer chains are cross-linked by methylene bridges[185,187]. The nature of the catalyst

¶ It has been found that, when formaldehyde and HCl interact in the gas phase, BCME is also formed[153–155].

† Chloromethylated polystyrene can also be obtained by the polymerisation of *p*-chloromethylstyrene[184].

has a significant influence on the rate of reaction and the degree of conversion of the copolymer, i.e. the average number of chloromethyl groups per benzene ring in the polymer molecule. Comparison of the degrees of conversion of the copolymer over a specified period, the effective rate constants, and the activation energies made it possible to arrange the catalysts investigated in the following sequence in terms of their activities [200]:

$$SnCl_4 > ZnCl_2 > AlCl_3 > SnCl_2 > FeCl_3 .$$

The introduction of various additivites into the reaction mixture ($SiCl_4$ [201] and $ZrCl_4$ [202]) increases significantly the degree of conversion of the copolymer. These additives apparently regenerate the catalyst during the reaction.

The use of chloromethyl ethers instead of formaldehyde and HCl in the examples considered here is due to the fact that the diffusion of the reactants into the polymer is of decisive importance for these reactions, which take place in a heterogeneous medium. At the same time the fact that under comparable conditions the chloromethyl ethers are apparently more reactive chloromethylating agents than formaldehyde and HCl may also play a role in other instances. For example, when an unpurified mixture of MCME and BCME in acetic acid was used, the chloromethylation of 2-pyrones was achieved for the first time [203,204]. On the other hand, chloromethylpyrones could not be obtained by treatment with paraformaldehyde in the presence of HCl or zinc chloride.

Substituents influence the rate of reaction of chloromethyl ethers in the same way as that of formaldehyde and HCl. In particular, substituents with the $+I$ effect accelerate the reaction; for example, the rate of chloromethylation of mesitylene with MCME is much higher than that of benzene [149]. As shown for isoxazole derivatives [205,206], the reaction is facilitated by the presence in the ring of substituents such as methyl or phenyl and in all cases the chloromethyl group is directed to the 4-position of the isoxazole ring, similarly to other electrophilic substitution reactions, for example, nitration and halogenation [207].

Similar results were obtained also in the chloromethylation of 2,1,3-thia- and selena-diazoles and their homologues [208-211]. The chloromethyl group enters the 4-position, as in chlorination [212,213]; the reaction is facilitated by the introduction of electron-donating groups and is hindered in the presence of electron-accepting substituents. The activating influence of the alkyl substituent has also been observed for a series of *N*-aryl-*N*-methylsulphonylanilides [214-217].

Phenols and alkylphenols are chloromethylated readily, but immediately undergo further condensation reactions [218, 219]. For this reason, it has so far been impossible to isolate chloromethylphenols. Romadane and coworkers [220,221] chloromethylated *p*-alkoxybenzenes by various methods and showed that the main reaction product is 2-alkoxy-5-alkylbenzyl chloride (96–99%), while a second isomer, 5-alkoxy-2-alkylbenzyl chloride, is formed in a yield of 1–4%.

When 4-alkylphenyl methyl carbonates are chloromethylated by MCME in the presence of $SbCl_5$ as the catalyst, a mixture of isomers with the chloromethyl group in the 2- and 3-positions is formed, with the former isomer predominating [222,223]. It was possible to obtain bischloromethyl derivatives of these compounds only by treatment with BCME and in the presence of $SbCl_5$ as the catalyst [224]. The introduction into the ring of substituents with the $-I$ effect and even more so the introduction of substituents with the $-I$ and $-M$ effects (for example, using CH_2O + HCl) [150] hinders further chloromethylation. Thus dichlorobenzenes are chloromethylated with much greater difficulty than monosubstituted derivatives [225-229]. The attempts to introduce the chloromethyl group into 5-nitrosalicylaldehyde by the usual methods were unsuccessful. The reaction proceeds only when an excess of $AlCl_3$ and MCME is used [230].

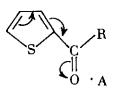
The chloromethylation of nitrobenzenes is carried out under severe conditions—by treatment with strong chloromethylating agents such as BCME and MCME and in the presence of strong inorganic acids. For example, when nitrobenzene is treated with BCME in 96% sulphuric acid (at 45–50°C for a week!), a 35% yield of *m*-nitrobenzyl chloride is obtained [231]. Berezovskii et al. [232] investigated the interaction of *p*-nitrotoluene with BCME and showed that, when the reaction is carried out in chlorosulphonic acid, or 5% oleum at a temperature not exceeding 10°C, the monochloromethyl derivative is obtained in an almost quantitative yield. An increase of temperature to 40–50°C and the use of 20–40% oleum or an excess of chlorosulphonic acid make it possible to introduce two chloromethyl groups into the *p*-nitrotoluene molecule. *p*-Ethylnitrobenzene gives 43% of 2-chloromethyl-1-ethyl-4-nitrobenzene and 10% of the corresponding 2,6-bischloromethyl derivative; *p*-isopropylnitrobenzene gives rise to monosubstituted products only, while *p*-t-butylnitrobenzene does not react at all [233]. The chloromethylation of phenols having deactivating substituents (the nitro-group or halogens) has been described in patents [234,235]. The reaction was carried out under different conditions: by treatment with bischloromethylether in sulphuric acid [234] and by treatment with mixture of 55% oleum and BCME. [235] The corresponding monochloromethyl derivatives were obtained in all instances. In the course of development of the synthesis of disubstituted tetrahydroisoquinolines, Beeby and Mann [236] obtained 2-(2-chloroethyl)-5-nitrobenzyl chloride as an intermediate, having treated 2-(*p*-nitrophenyl)ethyl chloride with BCME in the presence of 20% oleum. Under the influence of BCME in sulphuric acid, benzoic acid is converted into a mixture of *o*-, *m*-, and *p*-chloromethyl derivatives, with the *m*-isomer predominating [237] (see also Ref. 238). Under these conditions, alkylbenzoic acids give rise to bischloromethyl derivatives [239]. Chloromethyl derivatives of *N*-arylphthalimides have been obtained by treatment with BCME in concentrated sulphuric acid [240]; a patent [241] showed that indigo dyes can be mono- and di-chloromethylated. There have been a number of patents by the same investigators devoted to the chloromethylation of condensed systems deactivated by the carbonyl group [242-251]. The products of these reactions are of interest for the synthesis of dyes [244-247].

As in chloromethylation with formaldehyde and HCl (see above), on treatment with MCME the CH_2Cl group can be directed to the side chains of alkyl aryl ketones; the reaction is carried out in the presence of boron trifluoride etherate as the catalyst [252,253]. However, on treatment with MCME using an excess (2.5 moles) of aluminium chloride without a solvent [254] or under the influence of BCME in the presence of 1.4 moles of $AlCl_3$ in chloroform [255], the chloromethyl group enters the *m*-position of the benzene ring. Under these conditions, acetophenone exists in the form of a complex with $AlCl_3$, [256] which is the cause of the change in the mode of substitution. In the reaction involving complexes of 2-acylthiophens with $AlCl_3$, a change in the site where the CH_2Cl group is introduced into the thiophen ring is also observed. The chloromethylation of 2-acylthiophens by paraformaldehyde and HCl leads to the formation of a mixture of

4- and 5-chloromethyl derivatives in nearly equimolecular proportions [109-111]. The chloromethylation of thiophen-2-aldehyde and 2-acetothienone by MCME in the presence of 2.2 moles of $AlCl_3$ without a solvent or in chloroform yields 4-chloromethyl derivatives containing 7% and 2% of the 5-isomers respectively [110,257].

By carrying out the reaction in a solvent, it is possible to discover the essential features of the processes occurring, since there is the possibility of varying the amount of $AlCl_3$ (in experiments without a solvent, one must use more than 2 moles of $AlCl_3$ per moles of the carbonyl compound, since solid complexes are formed with small amounts of $AlCl_3$). In chloromethylation by treatment with MCME in the presence of comparatively small amounts of $AlCl_3$ in chloroform, the main reaction products are 5-substituted derivatives (70%, 90%, and up to 95% yields when 1.8, 1.3, and 0.9 moles of $AlCl_3$ are used respectively) [257]. This is undoubtedly caused by the dissociation of the complex of the carbonyl compound with $AlCl_3$ under the influence of MCME. The use of a weaker base (BCME) as the chloromethylating agent makes it possible to obtain 4-chloromethyl derivatives virtually without the 5-isomers even when the chloromethylation is carried out in the presence of 1.3 moles of $AlCl_3$. [257]

Thus, as in other electrophilic substitution reactions [258,259], the change in the mode of chloromethylation is a consequence of the formation of a 1 : 1 complex with $AlCl_3$ via the carbonyl group. By enhancing the electron-accepting capacity of the substituent, complex formation leads to such appreciable deactivation of the 5-position that the 4-position in the thiophen ring becomes the most reactive. This is confirmed by ^1H and ^{13}C NMR data for complexes of carbonyl derivatives of thiophen with $AlCl_3$. [256,260] The same effect, involving a change in the mode of electrophilic substitution, particularly in chloromethylation by chloromethyl ethers, is observed also when the carbonyl group is modified by protonation or complex formation with a strong protic acid [261,262]:



$A = AlCl_3$ or H^+.

One should note that the formation of a complex with aluminium chloride may influence the mode of substitution also in compounds with electron-donating substituents. Thus treatment of thioanisole with MCME in the presence of an excess of $AlCl_3$ leads to a high degree of selectivity with respect to the *p*-chloromethyl derivative. Nevertheless, in the presence of a deficiency of aluminium chloride, or when the reaction with MCME is carried out in acetic acid, or on chloromethylation by treatment with formalin and HCl, the product contains considerable amounts of the *o*-isomer (up to the equimolar ratio) together with the *p*-isomer [263].

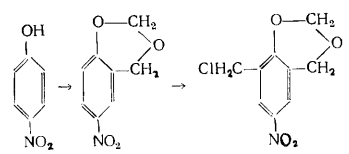
2. The Problem of the Mechanism of Chloromethylation by Treatment with Chloromethyl Ethers

In contrast to chloromethylation by treatment with formaldehyde and HCl, there are few kinetic data for the reactions of aromatic compounds with chloromethyl ethers in the literature. With the exception of the study [264] when the kinetics of the reaction of MCME with *p*-dichlorobenzene were investigated (however, unfortunately a detailed analysis of the mechanism in relation to the authors' kinetic data had not been carried out), the remaining investigations were devoted mainly to the study of the kinetics of the chloromethylation of polystyrene [265] or its copolymers [194,200]. The results thus obtained can be used only with important reservations, because, apart from the brief initial stage of the process, the rate of reaction is limited by the diffusion of the MCME–catalyst complex into the polymer

Two versions of the mechanism of the chloromethylation reaction involving chloromethyl ethers are possible. In the first, chloromethylation is preceded by the cleavage of the chloromethyl ether $ROCH_2Cl$ at the C–O bond under the influence of the protic or aprotic acid used as the condensing agent; the chloromethylating species is then the cation $\overset{+}{C}H_2Cl$. [261,264] In the second version the chloromethyl ether behaves as the alkylating agent, forming the cation $\overset{+}{C}H_2OR$ in the limiting case [187,257,262]. The alkoxymethyl derivatives formed are cleaved under the influence of the hydrogen chloride evolved and the aprotic acid (Verley [266]):

$$ArH \rightarrow ArCH_2OR \rightarrow ArCH_2Cl\ .$$

The reaction can proceed in principle simultaneously via two pathways or either pathway can predominate, depending on the conditions; however, the second pathway appears to be preferable. Indeed the alkylation of aromatic compounds by dialkyl ethers in the presence of Lewis acids takes place at elevated temperatures (of the order of 150–170°C), [267] i.e. under much more severe conditions than chloromethylation. Furthermore, MCME is known to be difficult to cleave by $AlCl_3$ (approximately to the extent of 3% after 100 h at 55°C), while BCME is still more stable [268]. On the other hand, chloromethyl ethers contain an exceptionally mobile halogen atom, capable of being exchanged via an S_N1 mechanism [269], which is probably associated with the stabilising effect of the oxygen atom on the cationic centre [270]. The formation of alkoxymethyl compounds noted above (see also Refs. 257, 263, 271, and 272) agrees with the second hypothesis. Since the alkoxymethyl derivatives are ethers of the benzyl type, they should be cleaved comparatively readily under the influence of $AlCl_3$ and HCl. [273,274] Indeed, additional treatment with hydrogen chloride and $AlCl_3$ of the reaction mixture obtained as a result of the interaction of 2-acetothienone with MCME in the presence of 1.3 moles of $AlCl_3$ lowers the content of 5-methoxymethyl-2-acetothienone approximately by a factor of two [257] (see also Belen'kii et al. [255]). When the reaction of 2-acetothienone with MCME is carried out in the presence of aluminium chloride etherate, i.e. under conditions promoting the cleavage of methoxymethyl derivatives by $AlCl_3$, the main product is a mixture of 4- and 5-methoxymethyl-2-acetothienones [257]. Topchiev and Stavrovskaya [275,276] showed that treatment of *p*-nitrophenol with BCME in the presence of $ZnCl_2$ entails initial alkylation and subsequent intramolecular ring closure and the formation of the methylene ether of 5-nitrosaligenin, which is then converted into the methylene ether of 3-chloromethyl-5-nitrosaligenin:



Thus the formation of chloromethyl derivatives when aromatic compounds are treated with chloromethyl ethers in the presence of $AlCl_3$ is the result of a multistage process, which may be represented by the following scheme:

$$ROCH_2Cl + AlCl_3 \rightleftarrows (ROCH_2)^+ AlCl_4^- , \quad (1)$$

$$ArH + (ROCH_2)^+ AlCl_4^- \rightleftarrows (ArHCH_2OR)^+ AlCl_4^- , \quad (2)$$

$$(ArHCH_2OR)^+ AlCl_4^- \rightarrow ArCH_2OR + HCl + AlCl_3 , \quad (3)$$
$$ArCH_2OR + AlCl_3 \rightarrow ArCH_2Cl + RCl + AlOCl , \quad (4)$$
$$ArCH_2OR + HCl \rightarrow ArCH_2Cl + ROH . \quad (5)$$

In the reactions with MCME and BCME, R = CH_3 and R = CH_2Cl or CH_2Ar respectively.

The process under consideration includes the formation of an electrophilic species [stage (1)], which is converted via a σ-complex [stage (2)] into a benzyl ether analogue $ArCH_2OR$ [stage (3)]; the latter gives rise to a chloromethyl derivative on cleavage under the influence of $AlCl_3$ [stage (4)] or HCl [stage (5)]. Nor can one rule out the possibility of the joint action of HCl and $AlCl_3$ on the ether with the intermediate formation of the protonated form $ArCH_2OHR^+.AlCl_4^-$.

The substances formed in stages (4) and (5) are the "normal" products of the cleavage of ethers by $AlCl_3$ [277] and HCl [273] (the cleavage of benzyl ethers by Lewis acids is also described by Gol'dfarb [278] and Stadnikov and Kashtanov [279]). If chloromethylation on treatment with BCME proceeds via the dibenzyl ether analogue $(ArCH_2)_2O$, then its cleavage by both an aprotic acid and by HCl should lead to the formation of two $ArCH_2Cl$ molecules [280]. The cleavage of an ether of the type $ArCH_2OCH_2Cl$ by HCl can lead to a chloromethyl derivative and the unstable chloromethanol $HOCH_2Cl$. The latter can function as a chloromethylating agent either directly or after dehydration with formation of BCME. Thus both CH_2Cl groups of the initial BCME can be used in the reaction [255,257].

However, the above mechanism does not provide a complete idea about the process considered, because it does not reflect the formation of diarylmethanes and bis-chloromethyl derivatives (for further details, see Belen'kii et al. [255]). In principle, the same mechanism is also probable when the reaction is carried out in strong inorganic acids. It has been shown [145] that alkyl chloromethyl ethers are protonated at the oxygen atom in an ultra-acidic medium and the protonated forms produced are dehydrochlorinated above −60°C, being converted into alkoxy-methyl cations‡:

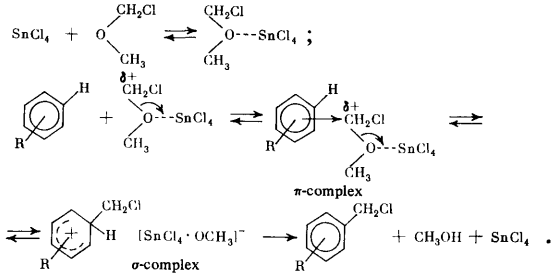
$$ClCH_2OR \xrightarrow[-80°]{FSO_3H-SbF_5} ClCH_2-\overset{+}{O}(H)-R \xrightarrow[-60°]{-HCl} CH_2=\overset{+}{O}R .$$

‡ A mechanism of a similar type has also been proposed [284] for chloromethylation and bromomethylation by treatment with 1-chloro-4-[chloro(bromo)methoxy]-butanes and 1,4-bis[chloro(bromo)methoxy]butanes, which have been recently described as effective halogenomethylating agents [285]. A characteristic feature of these substances is the possibility of the intermedite formation and involvement in the reaction of chloro-(bromo) methyltetrahydrofuranonium ions, which has been confirmed by the detection [284] with the aid of ^1H NMR of this type of ion, formed as a result of the following reaction at −50°C in SO_2:

$$ClCH_2O(CH_2)_4Cl + SbCl_5 \rightarrow ClCH_2-\overset{+}{O}\begin{matrix}CH_2-CH_2\\ |\\ CH_2-CH_2\end{matrix} SbCl_6^- .$$

The halogenoalkylation by these reagents proceeds with high yields in the presence of $SnCl_4$ or $ZnBr_2$. An advantage of these new agents over the less active BCME is a lower volatility and hence a smaller danger to the human organism [285].

A significant argument against the mechanism under consideration, involving attack by an alkoxymethyl cation, arises from the fact that the ion may react not only via the carbon atom with formation of an alkoxymethyl derivative but can also behave as a methylating agent (with liberation of formaldehyde) [281]. One can therefore consider a chloromethylation mechanism which does not provide for the formation of alkoxymethyl or chloromethyl cations and in which the chloromethylating species is a complex of the chloromethyl ether with a protic or aprotic acid. Mechanisms of this kind have been put forward in a number of studies [282,283]. In the relevant reports, it is postulated in essence that the CH_2Cl fragment from a complex of MCME and a Lewis acid enters into the aromatic ring. One of these mechanisms [283] is presented below:



If this or a similar mechanism is adopted, one cannot explain the formation of methoxymethyl derivatives discussed above. The reaction mechanism must apparently take into account both possible primary processes—chloromethylation and alkoxymethylation.

Despite the great importance of chloromethylation and its large-scale employment for preparative purposes, only partly described in this Review, many significant aspects of this reaction, associated primarily with its mechanism, have still been inadequately elucidated. This situation is apparently due to the great complexity of the process and its many pathways, as a result of which one can obtain, together with monochloromethyl derivatives, not only disubstituted derivatives but also products of another type—diarylmethanes and benzyl ethers. At the same time, the great scope of the synthesis based on chloromethyl derivatives led to the undertaking of further new investigations whose aim is both to modify the methods and to investigate the mechanism of the chloromethylation reaction.

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