Addition of tetrachloromethane to oct-1-ene initiated by amino alcohols

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The kinetics and mechanism of an addition of CCl_4 to oct-1-ene initiated by amines, aromatic alcohols, and amino alcohols (structural analogs of ephedrin) were studied. The radical mechanism of the reaction was established by ESR using the technique of spin traps. Aromatic amino alcohols as initiators are more active than amines and aromatic alcohols of similar structure. They are more selective compared to the amines and aromatic alcohols and react with CCl_4 already at room temperature to form predominantly benzaldehyde. The scheme of initiation by aromatic amino alcohols of the addition of CCl_4 to olefins was proposed on the basis of the experimental data.

Key words: radical addition, alkenes, oct-1-ene, carbon tetrachloride, 1,1,1,3-tetrachlorononane, 2-(*N*-methylamino)-1-phenylethanol, 2-(*N*-methylamino)-1-phenylpropan-1-ol, 1-phenylethanol, morpholine, *N*-methylphenethylamine.

The use of structural analogs of natural biologically active compounds capable of forming stable radicals under mild conditions is a possible way to create new initiating systems. It is known that ephedrin reacts with chlorine-containing organic compounds (for example, with $CHCl_3$) at room temperature to form species of radical nature.[1] It was of interest to use compounds, whose structures are close to the natural amino alcohol (ephedrin), as initiators of reactions involving CCl_4. Amines containing no functional groups initiate radical reactions of CCl_4 with hydrocarbons.[2] However, the efficiency of initiation is low even at high temperature, and no target products can be obtained in high yield. The initiating systems containing peroxide and organic reducing agents, in particular, amino alcohols and phosphites, were proposed for the reaction of CCl_4 with olefins; however, in this case, the yield of the addition product and selectivity are low.[3] In the present work, we used analogs of ephedrin, *viz.*, 2-methylamino-1-phenylethanol $PhCH(OH)CH_2NHMe$ (**1**) and 3-methylamino-1-phenylpropan-1-ol $PhCH(OH)CH_2CH_2NHMe$ (**2**), in the radical addition of CCl_4 to the double bond. Oct-1-ene was chosen as the model substrate, because the kinetics and composition of products of its interaction with CCl_4 in the presence of initiators of other types have been studied[4] in detail and help to judge about the reaction mechanism.

Experimental

Carbon tetrachloride (purity grade, additionally purified by distillation above P_2O_5, b.p. 76—77 °C), oct-1-ene (C_8H_{16}, Merck, distilled above metallic sodium *in vacuo*), and the following reagents (Sigma-Aldrich) were used: compounds **1** and **2**, *N*-benzyl-*N*-methylamine $PhCH_2NHMe$ (**3**), morpholine (**4**), 2-methyl-2-nitrosopropane $Bu^t—N=O$ (MNP), 2,2,6,6-tetramethylpiperidyl-*N*-oxide (TEMPO), 1-phenylethanol PhCH(OH)Me (**5**), benzoyl peroxide, and benzene (without additional purification). Purity of all compounds was checked by gas chromatography. Compound **5** was purified from peroxides by storage over cobalt stearate. The reaction was carried out in evacuated ampules (pressure not higher than 10^{-3} Torr) in the temperature interval from 80 to 130 °C using CCl_4 as the solvent. Organic products were analyzed by GLC using a Kristall 4000 chromatograph with a flame-ionization detector. GC-MS spectra were recorded on a Pye Unicam-104 chromatograph with an Ultra-1 column (length 25 m, inner diameter 0.2 mm, thickness of the liquid phase layer 0.33 μm); the chromatograph was connected with a Finnigan MAT ITD-700 ion trap. ESR spectra were recorded at 77 K on a Varian E-3 X-range radiospectrometer (high-frequency modulation 100 kHz) in thin-wall quartz ampules 4 mm in diameter. The *g* factor values were determined by the detection (simultaneously with recording ESR spectra of the studied substances) of hyperfine structure (HFS) components of the Mn^{2+} ions in MgO. The number of paramagnetic centers in the samples under study was determined by comparison of the surface areas under the absorption curves of the standard (single crystal $CuCl_2 \cdot 2H_2O$)

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and the studied sample reduced to equal detection conditions. The *S* values were determined using the authors´ program package and an automated system of data reception. The samples contained the initiator (0.1 mol L^{-1}) and MNP (0.1 mol L^{-1}) in a solution of CCl_4. Absorption spectra were recorded on a Shimadzu UV-320 instrument in the wavelength region from 200 to 800 nm. Samples were placed in a cell with a Teflon valve, and the mixture was liberated from dissolved gases in the same way as when preparing samples for ESR measurements.

Kinetic parameters were determined by the method of initial rates. It has preliminarily been shown that in the chosen condition range the kinetic curves had no inflections and no induction period was observed. To determine the reaction orders, the concentrations of the initiators and olefin were varied in the ranges 0.005—0.02 and 0.6—1.5 mol L^{-1}, respectively.

Results and Discussion

The reaction of CCl_4 with oct-1-ene in the presence of aromatic amino alcohols occurs mainly to form the addition product: 1,1,1,3-tetrachlorononane (**6**).

$$CCl_4 + H_2C{=}CH(CH_2)_5Me \rightarrow \underset{\mathbf{6}}{CCl_3CH_2CH(Cl)(CH_2)_5Me}$$

In addition to compound **6**, hexachloroethane and the product of allylic substitution 3-chlorooct-1-ene were found in insignificant amounts (at most 1—2%), as well as telomers that were not determined by GLC. Their total yield did not exceed 1%. The selectivity value was determined as the ratio of the yield of compound **6** to the total conversion of oct-1-ene. At the initial concentration of olefin 0.64 mol L^{-1} and a concentration of amino alcohol **1** of 0.015 mol L^{-1}, the reaction ceases in ~1 h (olefin conversion 37%). In the case of amino alcohol **2** under similar conditions, the reaction ceases in ~2 h (olefin conversion 34%), which is related to the consumption of the initiators. The reaction order was determined only from the initiator and olefin, because CCl_4 was used in more than twofold excess over olefin and a decrease in this ratio strongly changes the selectivity of the reaction: the yield of telomers increases multiply.

In excess CCl_4 the rate equation has the form

$$r = d[C_8H_{16}]/dt = k_{eff}[AA],$$

where AA is amino alcohol.

The zero order with respect to olefin indicates indirectly the radical mechanism of the reaction.[4,5] If the reaction proceeds *via* the coordination radical mechanism, the olefin concentration should enter into the kinetic equation. In this case, the kinetics is usually described by the first order with respect to olefin.

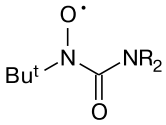
To reveal the nature of active species involved in the reaction, the ESR method with the technique of spin traps was used. The trap was MNP, which interacts with radicals to form spin-adducts **7**

$$Bu^t{-}N{=}O + R^{\cdot} \rightarrow \underset{\mathbf{7}}{Bu^t{-}N(O^{\cdot}){-}R}.$$

The formation of several spin-adducts was observed in all systems containing the initiator, CCl_4, and MNP. The initiator appears in the spectrum as a triplet with the HFC constant on the nitrogen nuclei a_N = 14.0 G, which corresponds to the parameters of the spin-adduct of the *tert*-butyl radical with the trap[6] formed due to the partial photolysis of the trap

$$Bu^t{-}N{=}O \xrightarrow[-NO]{h\nu} Bu^{t\cdot} \xrightarrow{MNP} Bu^t{}_2N{-}O^{\cdot}.$$

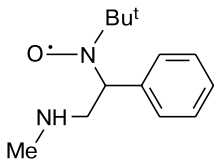
The second spin-adduct appears in the spectrum (Fig. 1, *a*) as a triplet of multiplets characterized by the triplet splitting constant a_N = 11.9 G and the multiplet splitting constant a = 2.3 G. The values of the splitting constants coincide with the constants of the spin-adducts of the $^{\cdot}CCl_3$ radicals with the trap.[6] Storage of the samples containing amines and amino alcohols at room temperature results in a change in the spectra and the appearance of a triplet with the constant a_N = 12 G (Fig. 1, *b*). Probably, the spin-adducts with the structure



formed from trichloromethyl-*tert*-butyl nitroxide correspond to this parameter.[7]

As can be seen from the data in Fig. 2, the kinetic curves of accumulation of the spin-adducts of the trap with the radical formed due to the reaction of the initiator with CCl_4 pass through a maximum or reach saturation. A decrease in the concentration of the spin-adducts is related to the consumption of the trap and adduct due to side reactions. The maximum concentrations of the spin-adducts with the trap and the initial rates of octene conversion referred to the initiator concentration are presented in Table 1. It is seen that the initiator activity correlates with the maximum concentration of the spin-adducts.

We detected the spin-adduct that appears in the spectrum as a triplet of doublets (Fig. 3) in addition to the mentioned spin-adducts in the system containing compound **3**. Its hyperfine triplet splitting constant on the nitrogen atom is a_N = 16.4 G, and the doublet splitting constant is a = 3.0 G. In this case, doublet splitting is the splitting on the hydrogen atom. The order of the HFC triplet constant indicates that the radical interacting with the trap increases the electron density on the nitrogen atom. Therefore, the radical contains a donor group, for in-



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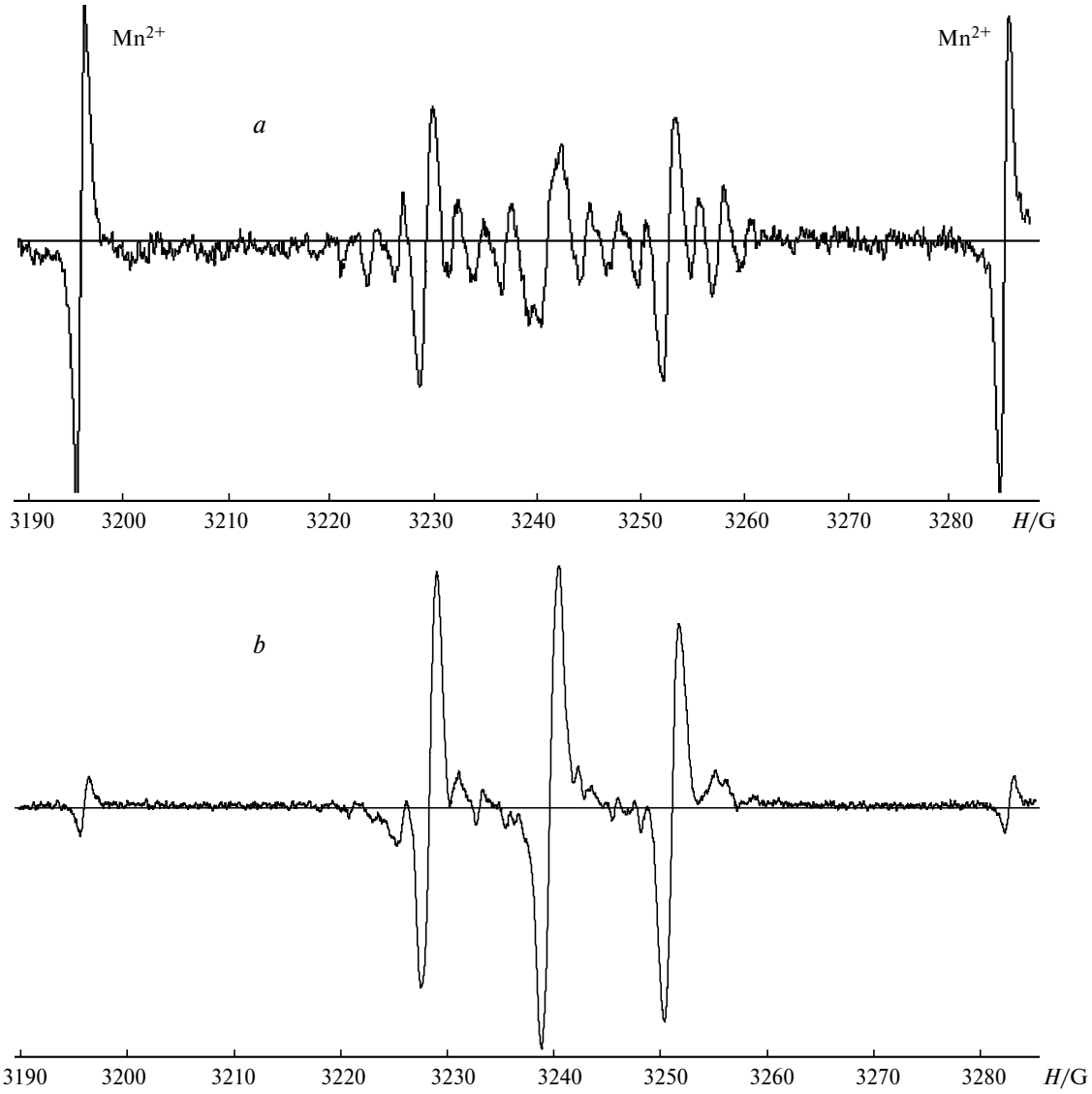


Fig. 1. ESR spectra of the CCl_4—MNP—**1** system 10 (*a*) and 60 min (*b*) after mixing the reactants at room temperature.

Table 1. Maximum concentrations of the spin-adducts with the trap and the initial concentration of octene conversion[a]

Initiator	$C \cdot 10^5$ /mol L^{-1}	T/°C	Conversion of olefin for 1 h (%)
Benzoyl peroxide	5.0	90[b]	33
1	9.0	130[c]	37
2	8.0	130[c]	22
3	0.7	130[c]	13

[a] Conditions: initiator concentration 0.015 mol L^{-1}, $[C_8H_{16}]$ = 0.64 mol L^{-1}, $[CCl_4]$ = 9.6 mol L^{-1}, 130 °C, 1 h.
[b] The conversion was measured by GLC from olefin consumption.
[c] The conversion was measured by GLC from the amount of the addition product that formed.

stance, benzyl or *tert*-butyl. This suggests that this signal is assigned to spin-adduct **8**.

Note that the detected maximum concentration of the spin-adducts is by several orders of magnitude lower than the concentrations of the trap and initiator. To prove that radical formation is not a side process, we carried out an analogous study using TEMPO as the trap.

It follows from the decay kinetics of TEMPO (Fig. 4) that its concentration decreases monotonically in the presence of both benzoyl peroxide and amino alcohol down to the considerable (more than 10%) degree of trap conversion. Thus, it can be asserted that the radicals are formed in a total amount comparable with the trap concentration and the interaction in the amino alcohol—CCl_4 system proceeds *via* the radical mechanism. The low concentration of the spin-adducts in the systems containing

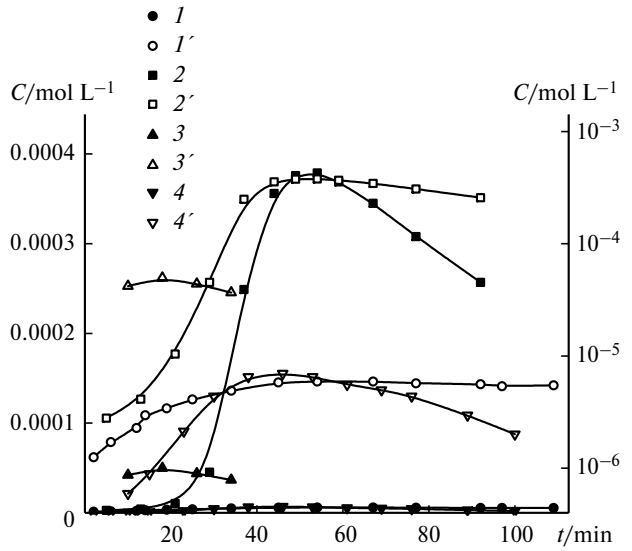


Fig. 2. Kinetics of changing the concentration of the spin-adducts with 2-methyl-2-nitrosopropane in the linear (*1*—*4*) and logarithmic (*1′*—*4′*) scales in the presence of different initiators: amino alcohol **2** (*1*, *1′*), amino alcohol **1** (*2*, *2′*), benzoyl peroxide (*3*, *3′*), and *N*-methylphenethylamine (*4*, *4′*).

MNP is caused by side reactions resulting in the decay of the trap and spin-adduct.

The consumption of MNP in the systems containing amino alcohols is clearly confirmed by the data of UV spectroscopy. The spectra of a solution of MNP in CCl_4 contain two bands: a low-intensity band at 675 nm (monomeric form) and an intense band at 260—270 nm (MNP dimer). After amino alcohol **1** was added, the intensity of the band of the monomer decreased by 30% during 4 h, and in 24 h it almost halved. Taking into account that the maximum yield of the spin-adducts with the $^{\bullet}CCl_3$ radicals is much lower than 30% (see Table 1), we can conclude that the decrease in their concentration is related to the consumption of MNP in side reactions. Since the spin-adducts are thermodynamically unstable and equilibrated with the trap,[8] the consumption of the trap leads to the decay of the spin-adducts. One of these reactions can be the interaction of MNP with HCl, which is incompletely bound with the remaining amino alcohol to the salt and is one of the reaction products of the amino alcohol with CCl_4. According to published data,[8] MNP decays rapidly in the presence of protic acids.

To evaluate the role of the nature of functional groups of the aromatic substrates used in the initiation of the reaction considered, we tested as initiators compounds containing only the benzylic hydroxy group (compound **5**) and, on the contrary, only the secondary amino group (morpholine **4** and amine **3**), as well as benzoyl peroxide. All these compounds manifested the initiating activity: the highest activity belongs to amino alcohol **1** and benzoyl peroxide, alcohol **5** and amine **3** have the lowest activity, and amine **4** and amino alcohol **2** are medium in this series (Table 2). The high selectivity was demonstrated by morpholine and both amino alcohols, and alcohol **5** and benzoyl peroxide are of low selectivity. Thus, the necessary condition providing a combination of high activity and selectivity of the initiator is the simultaneous presence of the alcohol and amine groups in its molecule.

The high selectivity of the reaction in the presence of amines is caused, most probably, by the fact that the

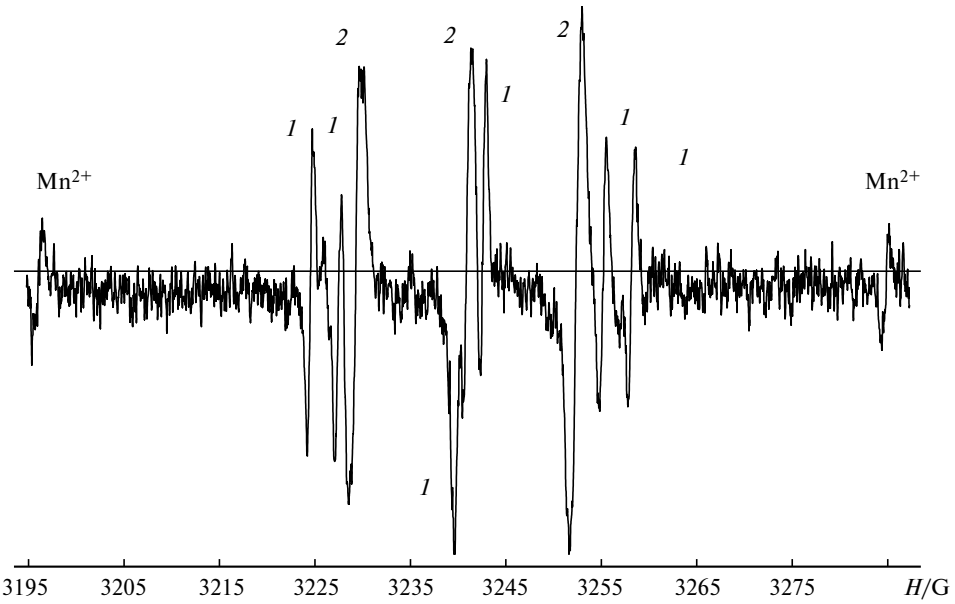


Fig. 3. ESR spectrum (recorded in the dark) of the system containing *N*-methylphenethylamine, carbon tetrachloride, and 2-methyl-2-nitrosopropane: *1*, substituted benzyl radical and *2*, amide radical.

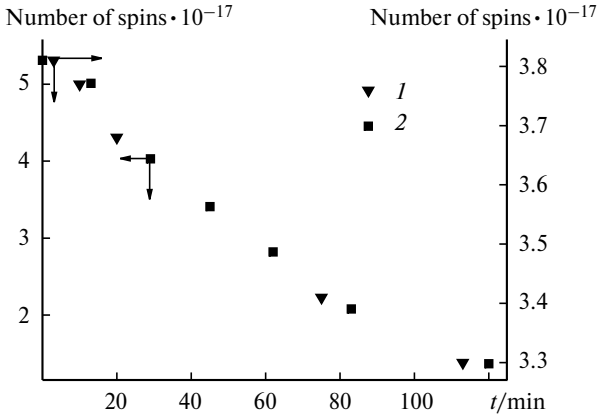


Fig. 4. Kinetics of TEMPO consumption in the presence of 2-(*N*-methylamino)-1-phenylethanol (*1*) and benzoyl peroxide (*2*).

Table 2. Activity of organic compounds in the addition of carbon tetrachloride to oct-1-ene[a]

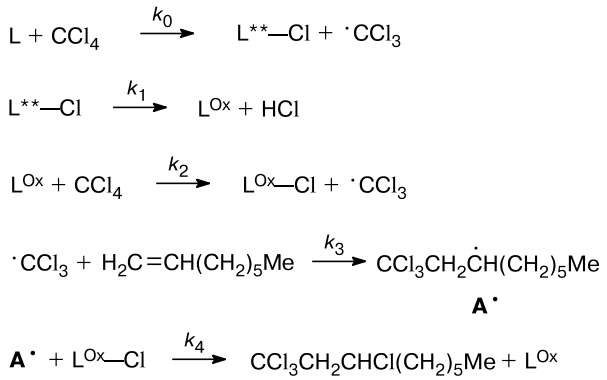
Initiator	Conversion[b] of olefin for 1 h (%)	A^c/h^{-1}	Selectivity[b] (%)
Benzoyl peroxide (90 °C)	34	15	30
1	35	15	95—100
2	22	9	95—100
3	13	6	87
4	19	8	98
5	14	6	34

[a] The conditions are presented in Table 1.
[b] The conversion of olefin and the selectivity of the process were determined by gas chromatography with internal standard.
[c] $A = r_0/[I]_0$ (I is initiator).

initiator is involved in chain transfer. A similar assumption has been advanced previously[9—11] when studying radical telomerization initiated by carbonyl and iron salts. It has been found[9—11] that small additives of secondary amines (and some other donors, in particular, isopropyl alcohol) increase sharply the yield of the addition product.

The following scheme of participation of aromatic amino alcohols in the reaction can be proposed on the basis of the obtained results. In the first step amino alcohol reacts with CCl_4 to form products of its oxidation (*N*-chloramine, α-chloramine, radical cation iminium salt) and $^{\bullet}CCl_3$ radicals. Similar reactions involving amines are described.[10,12] The $^{\bullet}CCl_3$ radical begins the kinetic chain from the addition to olefin affording the 1-trichloromethyloct-2-yl radical (**A**$^{\bullet}$), which eliminates the Cl atom from the oxidized molecule of the amino alcohol or from the CCl_4 molecule (Scheme 1).

Scheme 1



L^{Ox} is radical product of amino alcohol oxidation,
L^{Ox}—Cl is *N*-chloroamine or α-chloroamine

The mechanism presented in Scheme 1 in the approximation of the steady-state concentration method corresponds to the kinetic equation

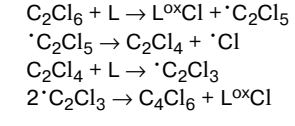
$$r = d[P]/dt = k_0[L][CCl_4],$$

where P is the product.

This equation satisfies the observed kinetics of the first order with respect to the initiator and the zero order with respect to olefin at $k_{app} = k_0[CCl_4]$. This scheme also explains the formation of the $^{\bullet}CCl_3$ radicals.

The nature of organic intermediates in the process can be judged from the GC-MS data. Heating a benzene solution of amino alcohol **1** at 100 °C for 1 h does not change its structure, indicating that this amino alcohol is stable under these conditions. Hexachloroethane, which is the dimerization product of the $^{\bullet}CCl_3$ radicals, is formed as the main product of the reaction of amino alcohol **1** with CCl_4 in the absence of olefin at 100 °C, whereas other chlorine-containing hydrocarbons, in particular, tetrachloroethylene and hexachlorobuta-1,3-diene, are formed in lower amounts (Scheme 2).

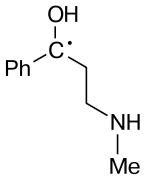
Scheme 2



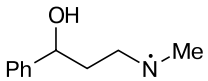
Amino alcohol **1** is mainly transformed into benzaldehyde and polymeric products, which are, probably, derivatives of enamine PhCH=CHNHMe. Amino alcohol **1** reacts with CCl_4 already at room temperature; CCl_4 is transformed into hexachloroethane and perchloroethylenes, and compound **1** is predominantly transformed into benzaldehyde and a complex mixture of products.

The reaction of compound **2** with CCl_4 at 100 °C affords chloroform, hexachloroethane, and tri- and

tetrachloroethylenes. Benzaldehyde is the main substance into which the initial amino alcohol is transformed. In addition, other carbonyl compounds (benzoyl chloride, methyl phenyl ketone PhCOMe, vinyl phenyl ketone $PhCOCH{=}CH_2$) were found in the system. All these compounds are, most likely, the products of rearrangement and decay of substituted benzyl radical **B**. In the systems under study, this radical can be formed due to the rearrangement of amine radical **C**.



B

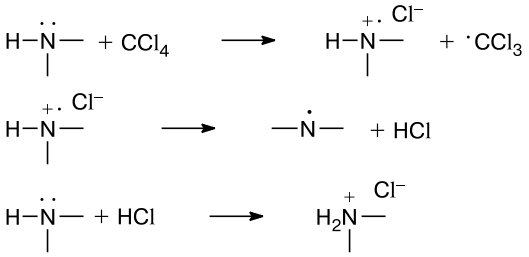


C

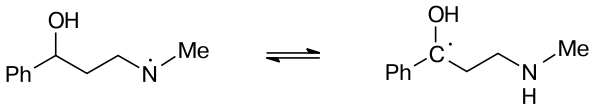
As already mentioned, the reactions of secondary and tertiary amines and aromatic amino alcohols (ephedrin and epiphedrin) with CCl_4 to form the trichloromethyl radical and HCl (which is bound by excess amine to insoluble dialkylammonium hydrochloride) have been described.[1,13] This reaction presumably proceeds through the step of formation of the radical cation iminium salt[14] (Scheme 3).

We believe that the amino alcohols under study react with CCl_4 similarly. At first CCl_4 oxidizes the amino alcohol to form the trichloromethyl and amine radicals. Probably, this process proceeds through the intermediate formation of the radical cation iminium salt, which eliminates hydrogen chloride (it is bound by excess amino

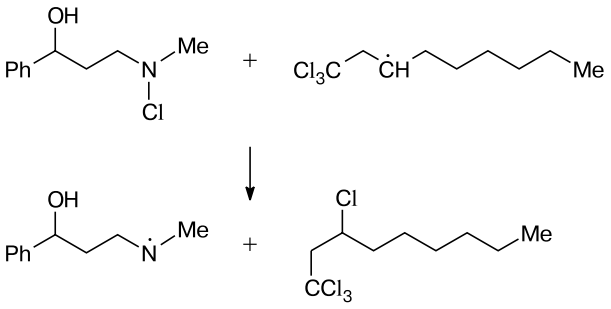
Scheme 3



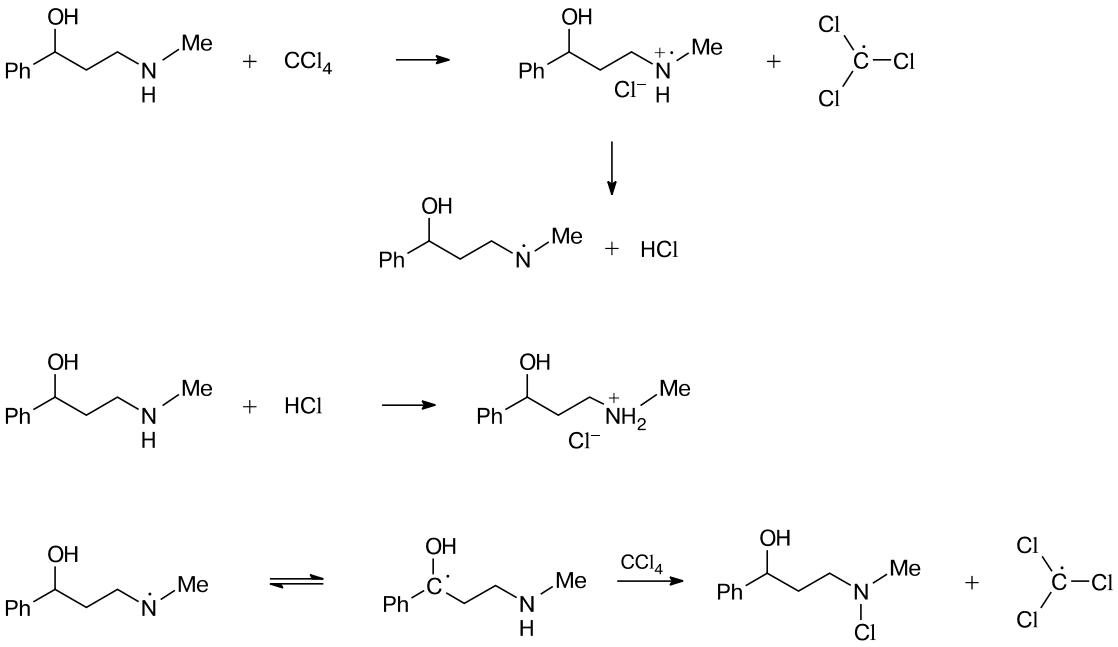
Scheme 4



Scheme 5



Scheme 6



alcohol to ammonium salt). In fact, when mixing the studied aromatic amino alcohols with CCl_4, we observed the formation of insoluble substituted ammonium hydrochloride. This process occurs especially rapidly in air. The amine radical can be rearranged to a more stable benzyl radical (Scheme 4).

Similar processes of hydrogen migration in radicals are well known.[13] The amine radical can eliminate the Cl atom from the CCl_4 molecule, being transformed into chloramine. The $^{\bullet}CCl_3$ radicals add to octene, and chloramine participates in chain transfer (Scheme 5).

The proposed mechanism is favored by the earlier presented data on the initiation of the addition reaction by amine **3**. The ESR analysis of this system showed the formation of the spin-adduct of MNP with the substituted benzyl radical (amine **3** differs from amino alcohol **2** only by the absence of the hydroxyl group). The higher activity of the aromatic amino alcohol can be due to a higher stability of the corresponding radical.

The probable step of initiation of the addition reaction in the presence of amino alcohols is presented in Scheme 6.

All the presented above processes provide the high efficiency of the aromatic amino alcohols in the initiation of the reaction of CCl_4 with olefins.

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