CONCLUSIONS

NMR spectroscopy was used to find the stereochemistry of a series of compounds with bicyclo[3.1.0]-hexane structure obtained from carane derivatives as a result of rearrangement with transannular participation of the cyclopropyl ring and the stereochemistry of this rearrangement was considered.

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OXIDATIVE CHLORINATION OF TOLUENE IN THE PRESENCE OF $CuCl_2$

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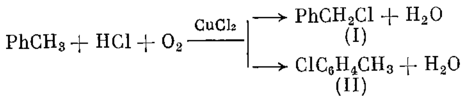
547.533

The reaction of toluene with HCl and O_2 at 300-510°C catalyzed by $CuCl_2$ on supports gives benzyl chloride (I) and chlorotoluenes (II) as the major products with low selectivity [1]



$$PhCH_3 + HCl + O_2 \xrightarrow{CuCl_2} \begin{cases} \underset{(I)}{PhCH_2Cl} + H_2O & (1) \\ \underset{(II)}{ClC_6H_4CH_3} + H_2O & (2) \end{cases}$$

This reaction is accompanied by the formation of a number of secondary products such as benzene and benzaldehyde [2]. The factors which affect the direction and selectivity of the oxidative chlorination of toluene have not been studied extensively. In addition, much remains unclear concerning the participation of $CuCl_2$ in the conversion of the reagents.

In the present work, we studied the effect of the reaction conditions on the direction and selectivity of the oxidative chlorination of toluene in the presence of $CuCl_3$ supported on heat-treated Al_2O_3 with specific surface 1 m^2/g. A high specific surface of the supports (above 10 m^2/g) causes rapid combustion of toluene.

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TABLE 1. Composition of the Products of the Vapor-Phase Chlorination of Toluene in the Side-Chain (2% $CuCl_2$ relative to the weight of Al_2O_3)

Type and conditions of toluene chlorination (contact time)	Product composition, %								
	$PhCH_2Cl$	$PhCHCl_2$+ +$PhCCl_3$	$ClC_6H_4CH_3$+ +$Cl_2C_6H_3CH_3$	PhH	PhCl	PhCHO	$PhCH_2CH_2Ph$	PhCH=CHPh	other products
Direct thermal chlorination in the bulk, toluene/Cl_2 = 1 : 1, glass packing (0.8 sec)	59,1	8,9	29,7	–	–	–	1,1	0,4	0,8
Direct thermocatalytic chlorination, toluene/Cl_2 = 1 : 1 (0.2 sec)	76,8	1,1	19,4	0,5	0,2	–	0,7	0,3	1,0
Oxidative chlorination, toluene/HCl/O_2 = 1 : 1 : 0.5 (2 sec)	80,7	0,5	13,0	2,7	1,1	0,8	0,5	0,3	0,4
Chlorination by means of $CuCl_2$ (2 sec)	81,1	0,3	17,0	0,3	–	–	0,2	0,1	1,1

TABLE 2. Composition of the Products of the Vapor-Phase Chlorination of Toluene in the Aromatic Ring (380°C, 10% $CuCl_2$ relative to the weight of Al_2O_3)

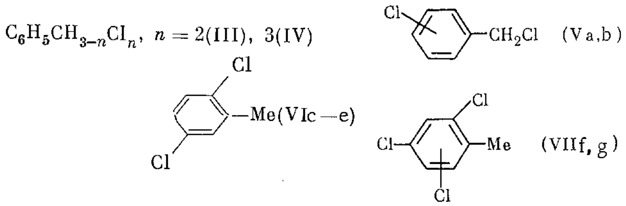
Type and conditions of toluene chlorination (contact time)	Product composition, %									
	4-$ClC_6H_4CH_3$	2-$ClC_6H_4CH_3$	3-$ClC_6H_4CH_3$	$C_6H_3Cl_2CH_3$	$C_6H_2Cl_3CH_3$	$PhCH_2Cl$	PhH	PhCl	$(CH_3C_6H_4)_2$	other products
Direct thermal chlorination in the bulk, toluene/Cl_2 = 1 : 2, glass packing (1.2 sec)	18,1	22,6	3,5	39,5	2,0	10,3	–	–	1,8	2,2
Direct thermocatalytic chlorination, toluene/Cl_2 = 1 : 2 (0.3 sec)	33,3	24,1	–	32,7	1,5	5,2	0,5	0,3	0,8	1,6
Oxidative chlorination, toluene/HCl/O_2 = 1 : 2 : 1 (2 sec)	32,5	25,3	–	30,4	1,2	6,6	0,4	0,4	1,2	2,0
Chlorination by means of $CuCl_2$ (2 sec)	31,2	23,0	–	34,9	1,4	5,9	0,5	0,4	0,9	1,8

TABLE 3. Effect of Added Nitrobenzene in Various Types of Vapor-Phase Chlorination of Toluene in the Aromatic Ring (10% $CuCl_2$ relative to the weight of Al_2O_3, 0.5% nitrobenzene relative to the weight of toluene)

Type and conditions of toluene chlorination (contact time)	Product composition %		Toluene composition, %	
	$ClC_6H_4CH_3$	other products	without added nitrobenzene	with added nitrobenzene
Direct thermal chlorination in the bulk, toluene/Cl_2 = 1 : 2, glass packing (1.2 sec)	40,5	59,5	40,3	19,5
Direct thermocatalytic chlorination, toluene/Cl_2 = 1 : 2 (0.3 sec)	54,3	45,7	80,7	70,9
Oxidative chlorination, toluene : HCl : O_2 = 1 : 2 : 1 (2 sec)	55,7	44,3	49,0	39,2
Chlorination by means of $CuCl_2$ (2 sec)	53,9	46,1	9,5	8,0

A low $CuCl_2$ content (1-2% of the weight of Al_2O_3) provides for high selectivity relative to (I) and an increase in the $CuCl_2$ content leads to 10-11% (II). For 2-3 sec contact time, the range from 460° to 470° is most favorable for reaction (1) while the range from 370° to 380°C is most favorable for reaction (2).

In addition to the products of reactions (1) and (2), we isolated dichloromethylbenzenes (III), trichloromethylbenzenes (IV), 2-chloro- (Va) and 4-chlorobenzyl chlorides (Vb), dichlorotoluenes (VIc-e), and trichlorotoluenes (VIIf, g)*


$C_6H_5CH_{3-n}Cl_n$, $n = 2$(III), 3(IV)

In addition, we identified the products of the oxidation of toluene (benzaldehyde, benzyl alcohol, dibenzyl ether, and phenol), benzene, chlorobenzene, dibenzyl, stilbene, dimethylbiphenyls and gaseous products Cl_2, CO_2, and CO.

The optimal $PhCh_3 : HCl : O_2$ ratio was the stoichiometric ratio. A $HCl : PhCH_3$ ratio above 2 at 460-470°C increases the yield of oxygen-containing products, benzene, chlorobenzene, and other products but at 370-380°C, such an increase is not found.

According to Suvorov and Bukeikhanov [3], the formation of Cl_2 in the $HCl-O_2$ system is a consequence of the oxidation of HCl. Another possible source of Cl_2 may be $CuCl_2$

$$2CuCl_2 \rightarrow 2CuCl + Cl_2 \qquad (3)$$

Determination of the rates of reaction (3) (0.13 mole/liter catalyst · h) and HCl oxidation (12.2 mole/liter catalyst · h) (450°C, 2% $CuCl_2$ on Al_2O_3) showed that the thermal decomposition of $CuCl_2$ does not play a significant role in the reaction.

The Cl_2 formed likely chlorinates toluene on the catalyst and in the bulk

$$PhCH_3 + Cl_2 - \begin{cases} \rightarrow (I) + HCl & (4) \\ \rightarrow (II) + HCl & (5) \end{cases}$$

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* The letter indices in (V)-(VII) correspond to the following chlorine atom positions: a) 2, b) 4, c) 2, 4, d) 2, 5, e) 2, 6, f) 2, 4, 5, and g) 2, 4, 6.

The hydrogen in the toluene theoretically may be substituted by a halide also by direct halogenation with $CuCl_2$ [3]. The reaction conditions and product compositions indicate that the oxidative chlorination of toluene in the side-chain proceeds with the formation of a benzyl radical.

In order to clarify the mechanism for the formation of (I) and (II), we studied the composition of the products of toluene chlorination under conditions for the reaction proceeding in the bulk and involving $CuCl_2$. The reactions involving $CuCl_2$, in contrast to the chlorination of toluene in the bulk, are characterized by a similar composition and ratio of products as well as enhanced selectivity relative to (I) (Table 1). The formation of $Ph\dot{C}H_2$ and its conversion to (I) occur in this case apparently according to the scheme [4-6]

$$PhCH_3 + CuCl_2 \rightarrow Ph\overset{+}{C}\dot{H}_3 + Cu(I)Cl + Cl^-$$
$$Ph\overset{+}{C}\dot{H}_3 \rightarrow Ph\dot{C}H_2 + H^+$$
$$Ph\dot{C}H_2 + Cl_2 \rightarrow (I) + Cl^{\cdot}$$
$$PhCH_3 + Cl^{\cdot} \rightarrow Ph\dot{C}H_2 + HCl$$
$$Ph\dot{C}H_2 + CuCl_2 \rightarrow (I) + CuCl$$

The reactions of the benzyl radicals are indicated by our results for the reaction of toluene with $CuCl_2$ under conditions analogous to the oxidative chlorination of toluene in the side-chain when $Ph\dot{C}H_2$ is generated from toluene thermally in the heating element and these radicals come into contact with $CuCl_2$.

We should note that the oxidative chlorination of toluene in the side-chain leads to the same products ($PhCH_2Cl$, PhCHO, and $PhCH_2CH_2Ph$) as in the liquid-phase oxidation of toluene by Cu(II) compounds [6].

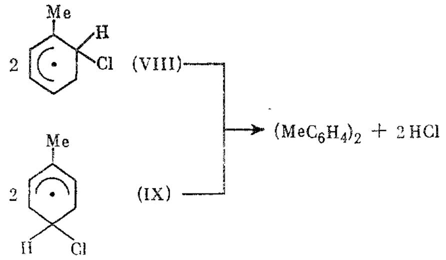
The oxidative chlorination of toluene in the ring, including the reaction catalyzed by $CuCl_2$, is characterized by an enhanced para direction, the absence of meta isomer, and high selectivity relative to (II) (Table 2). The reactivity of toluene and benzene in this reaction differs from their reactivity in the liquid-phase direct catalytic chlorination. Thus, at 280°C, C_6H_6 yields dichlorobenzenes in 70% yield and higher [7, 8] while toluene yields 2-(IIa) and $4\text{-}ClC_6H_4CH_3$ (IIb) in 7-8%; the yield of (II) reaches 40% and higher only at 380°C [9]. These findings indicate different mechanisms for the ring chlorination of toluene and benzene.

The radical nature of the oxidative ring chlorination of toluene is indicated by experiments with added nitrobenzene (Table 3) in light of the inhibiting effect of nitrobenzene on this reaction as well as on the $CuCl_2$-catalyzed chlorination of toluene.

The oxidative ring chlorination of toluene probably proceeds through σ-complexes of toluene with a chlorine atom (VIII) and (IX) whose formation is energetically more favorable than the tolyl radical [10].

The presence of dimethylbiphenyls in the products of all the vapor-phase ring chlorination (see Table 2) is an indirect indication of the existence of such complexes.

Similar complexes are apparently also obtained in the direct reaction of toluene with the catalyst as indicated by the formation of o- and p-bromotoluenes at the onset of the oxidative chlorination of toluene catalyzed by $CuBr_2$.



Complexes (VIII) and (IX) are converted by the action of $CuCl_2$ to (II) by means of a chlorine transfer from $CuCl_2$ to the complexes and stabilization of the oxidation product by HCl elimination [5]

$$(VIII) + CuCl_2 \rightarrow (IIa) + CuCl + HCl$$
$$(IX) + CuCl_2 \rightarrow (IIb) + CuCl + HCl$$

EXPERIMENTAL*

The catalyst was prepared by impregnation of silicon carbide (2-3 mm fraction) by an aqueous solution containing the calculated amount of metal chloride.

The vapor-phase chlorination of toluene was carried out according to our previous procedure [11]. Dimethylbiphenyls were obtained from the catalysate; 2- and 4-$BrC_6H_4CH_3$ were isolated in special experiments. The remaining products were identified by gas–liquid chromatography on an LKhM-72 chromatograph with a katharometer flow-meter and hydrogen gas carrier using a 3 m × 3 mm stainless steel column packed with 20% FM-16 oil on INZ-600 and with 1,2,3-tris(2-cyanoethoxy)propane on Chromaton N-AW.

The gaseous reaction products were analyzed by gas–liquid chromatography on a KhL-6 chromatograph with a katharometer flow-meter and nitrogen gas carrier on 3 m× 3 mm columns packed with 30% dibutyl phthalate on Poropack Q and 4 m × 3 mm columns with NaX sieves.

The compounds obtained were identified by comparison with the corresponding reference samples prepared by known methods.

CONCLUSIONS

1. The oxidative chlorination of toluene in the presence of $CuCl_2$ proceeds concurrently in the side-chain and in the aromatic ring. The direction of the reaction is determined by the temperature, reagent ratio, and amount of $CuCl_2$.

2. The chlorination of the toluene side-chain is accompanied by the formation of 1,2-diphenylethane and has a composition similar to the chlorination products of toluene by $CuCl_2$, $ClC_6H_4CH_3$ (II). The replacement of hydrogen by a halide in the aromatic ring proceeds predominantly in the para position and is inhibited by nitrobenzene.

3. Reaction schemes were proposed entailing the formation of the benzyl radical and σ-complexes of toluene with a chlorine atom which are converted into chlorinated products by the action of chlorine and $CuCl_2$ (II).

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