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Reactions of Long-Chain Chloro Alcohols or Unsaturated Alcohols with Benzene by Aluminum Chloride Catalyst

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Received December 12, 1977

A study was made of the reactions of 2-, 4-, and 5-chlorooctan-1-ols, 2-chlorohexan-1-ol, or 4- and 7-octen-1-ols with benzene in the presence of an excess of aluminum chloride catalyst. Isomeric x-phenylalkan-1-ols were obtained from both types of alcohols, but the isomer distributions differed considerably depending on the starting compounds. 2-Chloroalkan-1-ol yielded x-phenylalkan-1-ols (x is between 2 and the penultimate carbon number), but neither 2- nor 3-phenyloctan-1-ol was detected from the reactions of a mixture of 4- and 5-chlorooctan-1-ol or reactions of 4- and 7-octen-1-ol. Both the cation isomerization and phenyl migration toward the 2 or 3 position, close to the terminal substituent ($OAlCl_2$), were considered unlikely to occur. From the fact that the ratios of 6-/7-phenyl isomers in the product distributions were similar to those of 3-/2-phenyloctanes in the reaction product of octyl halide with benzene, the terminal functional group is presumed to hardly affect these remote positions.

Numerous reports have been published on Friedel–Crafts alkylation, and recently extensive studies have also been done on the reactions using long-chain alkylating agents which yield many isomeric products. These studies are well summarized in the preface of the report recently published by Roberts, McGuire, and Baker.[1] There are some reports on Friedel–Crafts reactions using long-chain compounds which contain functional groups,[2] such as carboxyl, carbonyl, and nitrile groups; however, little information is available for the reactions with alcohol derivatives except for lower halohydrin compounds.[3]

We have already reported that Friedel–Crafts reaction of 1,2-epoxyoctane with benzene in the presence of an equimolar amount of aluminum chloride catalyst produced 2-phenyloctan-1-ol as the main product,[4] and that the reaction catalyzed by an excess (1.5 mol) amount of aluminum chloride produced a mixture of phenyloctan-1-ol isomers.[5] This isomeric mixture is thought to be produced from 2-chlorooctan-1-ol which was formed by reaction of 1,2-epoxyoctane with the excess catalyst. Moreover, the isomer distribution of the products seemed to be affected by the terminal polar group. In this paper, we report results of Friedel–Crafts reactions of long-chain chloroalkan-1-ols or octen-1-ols with benzene in the presence of excess aluminum chloride, carried out in order to investigate how the isomer distribution is affected by the terminal polar group in long-chain alkylating agents.

Results and Discussion

In the reaction of an alcoholic compound with aluminum chloride catalyst, one molar amount of the catalyst is consumed by the hydroxy group.[3] In this work, then, the catalyst used was 1.5 times the molar quantity of the alcohol in each reaction.

Reaction of 2-Chlorooctan-1-ol. 2-Chlorooctan-1-ol (0.02 mol) was added to a suspension of aluminum chloride (0.03 mol) in benzene (0.4 mol). The mixture was allowed to react

at 5 °C, and the isomer distribution of the reaction products after various reaction times was determined by gas chromatography (GC).

The secondary chloride was substituted by a phenyl group in preference to the terminal hydroxy group, which remained apparently unchanged. A mixture of isomeric x-phenyloctan-1-ols (x is between 2 and 7) was obtained in fairly high yield suggesting no major side reactions occurred under the conditions used to develop the data shown in Table IA.

It was found that a higher yield of 7-phenyloctan-1-ol was obtained than any of the other isomers, and that the total amount of 2- and 3-phenyloctan-1-ols was the lowest in product distribution. These latter two isomers were not separable from each other by GC even after being converted to their trimethylsilyl ethers. However, the content of 2-phenyl isomer was presumed to be less than that of 3-phenyl isomer from a consideration of the results of the reaction with 2-chlorohexan-1-ol, in which the 2-phenyl isomer was found to be produced in lesser amount than the 3-phenyl isomer.

Friedel–Crafts reactions of arenes with long-chain alkylating agents generally involve various reaction processes, such as isomerization of intermediate ions, ion attacks on the arene, or isomerization and transalkylation of the products. In this work, therefore, the following experiments were carried out to confirm the results shown in Table I. Although 3-phenylhexan-1-ol was added as a tracer with the catalyst (1:1.5) to a reaction of 2-chlorooctan-1-ol with benzene catalyzed by aluminum chloride, the tracer compound did not isomerize to other phenylhexan-1-ols after 4.5 h at 5 °C; however, 4- and 5-phenylhexan-1-ols were detected after an additional several hours at 40 °C. 2-Phenyloctan-1-ol did not isomerize after being treated with benzene for 5 h at 5 °C in the presence of 1.5 mol of the catalyst. As mentioned later, isomerization of the products, even if it occurred among 4- to 7-phenyl isomers, occurred only very slowly at this temperature. The starting chloro alcohol was not isomerized under these reaction con-

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Table I. Product Distribution in Reaction of 2-Chlorooctan-1-ol[k] with Benzene[l] at 5 °C (A) and 30 °C (B)

reaction time, h	conversion, %	yield, %[a]	2-,[e] 3-[f]	4-[g]	5-[h]	6-[i]	7-[j]
			*x*-phenyloctan-1-ols, %, *x* =				
		A					
1	24	13	10	20	22	19	29
2	41	40	11	21	21	19	28
3	59	55	11	21	21	19	28
5	92	91	11	21	19	19	30
9	100	98	11	21	19	19	30[b]
		B					
0.5	64	60	9	20	22	19	30
1	100	90	9	19	20	19	33[c]
2		62	19[d]	18	16	16	31

[a] Based on the used chloro alcohol. [b] 6- to 7-isomer ratio = 0.63. [c] 6- to 7-isomer ratio = 0.58. [d] Total amount of 2 and 3 isomers at 100% conversion was not changed during the reaction period up to 8.5 h. [e] Registry no. 21078-90-0. [f] Registry no. 53118-85-7. [g] Registry no. 53118-86-8. [h] Registry no. 67700-19-0. [i] Registry no. 67700-20-3. [j] Registry no. 67700-21-4. [k] Registry no. 19472-94-7. [l] Registry no. 71-43-2.

ditions, based on GC analysis of recovered chloro alcohol as was similarly described in a previous report.[6]

In Table IA, no marked change is observed in product distribution after various reaction periods, suggesting that significant isomerization of the products did not occur under these reaction conditions. Therefore, the product distributions obtained may be regarded as indicative of a distribution of positive charges located at the 2 to 7 positions. Presumably the 2- to 7-phenyl isomers were produced from the corresponding 2 to 7 cations, and not from the 2-phenyl isomer. The fact that 2- and 3-phenyl isomers were produced in smaller quantities than were 4 to 7 isomers suggests that the cation initially formed at the 2 position isomerizes to more stable isomeric cations in which the positive charge locates beyond the 3 position, where the electron-withdrawing effect of the terminal polar group (–OAlCl₂) falls off.

After 2-chlorooctan-1-ol was completely consumed in the reaction at 30 °C, the total yield of *x*-phenyloctan-1-ols decreased and the distribution changed. The absolute yield of 2- and 3-phenyl isomers remained almost unchanged, although the relative quantity increased as a result of the consumption of 4- to 7-phenyl isomers by dealkylation or transalkylation (Table IB). To confirm these side reactions, a mixture of 2- to 7-phenyloctan-1-ols was treated with toluene in the presence of an excess of the catalyst (Table II). A decrease in quantity of 4 to 7 isomers was observed even at 5 °C (not noticeable in the reaction with benzene), and this decrease became extremely noticeable at 30 °C. However, the total yield of 2 and 3 isomers only slightly decreased at the same temperature. Dealkylation or transalkylation appears also to take place more readily at positions away from the functional group than at the 2 and 3 positions. Presumably

polarization of the phenyl–alkyl bond does not take place at closer positions to the electron-withdrawing group. This assumption is supported by the above-mentioned fact that the phenyl group of the 2 or 3 isomer hardly migrates toward the remote positions, even though they are less influenced stereochemically by the terminal substituent.[2a]

Reaction with a Mixture of 4- and 5-Chlorooctan-1-ols. A similar reaction was carried out using a mixture of 4- and 5-chlorooctan-1-ols (23:77). These chlorooctan-1-ols tended to react more readily with benzene than 2-chlorooctan-1-ol did, and 5-chlorooctan-1-ol was converted somewhat more rapidly than was 4-chlorooctan-1-ol (Table III).

Results in Table III show the distribution of products obtained in a comparatively short reaction time. There was a tendency for a large quantity of 6- and 7-phenyl isomers to be obtained at an early stage of the reaction whereas 2- and 3-phenyl isomers were not produced at the same stage. The cations produced at the 4 or 5 position readily isomerized to the more favorable 6 and 7 cations, but not to the 2 or 3 cation. Since no significant change was observed in the product distribution at early stages of the reaction, attack by the ions on benzene appeared to take place after rearrangement of the cations. After complete conversion of the starting chlorooctan-1-ols, isomerization of the phenylated products occurred gradually to give the 4-phenyl isomer, but still no 2 or 3 isomer was obtained; during this same period the relative ratios of the 5, 6, and 7 isomers tended to approach a corresponding value to that obtained from the reaction of 2-chlorooctan-1-ol (Table IA).

Reactions with 4-Octen-1-ol and 7-Octen-1-ol. It was found that 5- and 7-phenylated compounds were the major products, respectively, of similar reactions with 4- and 7-

Table II. Changes in Distribution of *x*-Phenyloctan-1-ols by Treatments with Toluene and Aluminum Chloride at 5 °C (A) and 30 °C (B)

reaction time, h	amount of *x*-phenyloctan-1-ols (initial = 1)	2-, 3-	4-	5-	6-	7-
		*x*-phenyloctan-1-ols, %, *x* =				
		A				
0	1.00	11	21	19	19	30
3	0.84	11	21	18	14	20
8	0.58	11	19	14	7	7
23	0.44	11	18	12	2	1
		B				
0	1.00	11	21	19	19	30
0.5	0.43	10	18	11	4	0
1.5	0.22	9	13	0	0	0
3.5	0.17	9	8	0	0	0

Table III. Product Distribution in Reaction of a Mixture of 4- and 5-Chlorooctan-1-ols (23:77) with Benzene at 5 °C

reaction time, min	conversion, %		Yield, %		x-phenyloctan-1-ols, %,[b] $x =$			
	4-	5-	calcd[a]	obsd	4-	5-	6-	7-
0.5	0	19	15	10	1	15	32	52
1.5	7	50	40	31	1	15	31	53
2.5	31	73	63	52	1	15	31	53
3.5	55	89	84	81	2	15	30	53
5.0	93	100	98	95	3	15	29	53
300	100		100	93	17	23	22	38[c]

[a] Calculated based on the conversions of 4- and 5-chlorides. [b] Isomers of 2 and 3 were not obtained. [c] 6- to 7-isomer ratio = 0.58.

Table IV. Product Distribution in Reaction of 4-Octen-1-ol (A) or 7-Octen-1-ol (B) with Benzene at 5 °C

reaction time, h	conversion, %	x-phenyloctan-1-ols, %,[a] $x =$			
		4-	5-	6-	7-
		A			
0.25	11	5	42	23	30
0.5	38	5	42	23	30
1	100	5	41	24	30
2		5	35	23	37
4		4	34	25	37
6		6	32	24	38
16		7	23	26	44
24		9	22	25	44[b]
		B			
0.3	51	2	4	30	64
0.7	72	2	5	32	61
1	100	3	7	30	60
3		5	8	28	59

[a] Isomers of 2 and 3 were not obtained. [b] 6- to 7-isomer ratio = 0.57.

octen-1-ols catalyzed by aluminum chloride (hydrogen chloride was not added) (Table IV).

Results in Table IVA indicate that an alteration of hydroxyalkylating agent brought about a different distribution from that obtained from the reaction with the mixture of 4- and 5-chlorooctan-1-ols (Table III). Between both reaction systems with different cation sources, the product distributions should not be simply compared because the systems include several different factors in reaction processes, such as formation of ions, acidity of the systems,[7] kind of counter ions,[8] and so on. Still, the nonconformity of both distributions at early stages of the reaction is considered to be due to the fact that the rate of the alkylation step is not sufficiently slow[9] so that isomerization of the intermediate cations is not allowed to proceed to completion. One can see here an example of the results influenced by a cation source as pointed out by Roberts at al.[1] After both unsaturated alcohols were almost completely consumed, the products seemed to rearrange gradually to an equilibrium distribution, and the amount of 4-phenyl isomer seemed to approach a value similar to the relative quantity in Table III.

Ansell[2a] reported that a reaction of 8-nonenoic acid with benzene under drastic conditions (reflux, 16 h) afforded 5-phenylnonanoic acid as the product phenylated at the nearest position to the polar group. Four[2c] also reported that the 5-phenyl isomer was obtained similarly in a reaction of 7-octenoic acid. In our work the 4-phenylated product was obtained under relatively mild conditions. This is thought to be because the degree of the influence on the 4 position by both the steric factor and electron-withdrawing property is lower with the terminal oxyaluminum dichloride than with the carbonyloxyaluminum dichloride.[10]

Reaction of 2-Chlorohexan-1-ol. Four isomers of x'-phenylhexan-1-ols (x' is 2 to 5) were obtained from reaction

Table V. Product Distribution in Reaction of 2-Chlorohexan-1-ol[e] with Benzene at 20 °C

reaction time, min	conversion, %	yield, %	x-phenylhexan-1-ols, %,			
			2-[a]	3-[b]	4-[c]	5-[d]
40	40	31	2	10	23	65
80	93	62	2	10	24	64
130	100	76	1	9	29	61

[a] Registry no. 25755-73-1. [b] Registry no. 67700-22-5. [c] Registry no. 67700-23-6. [d] Registry no. 28591-17-5. [e] Registry no. 63216-75-1.

of 2-chlorohexan-1-ol with benzene at 20 °C, and they were separated and determined by GC (Table V).

The total yield was comparatively lower than that of the phenyloctan-1-ols, and a slight change in product distribution was observed. This probably stems from dealkylation or transalkylation occurring at this higher reaction temperature. As to the reaction of 2-chlorohexan-1-ol, it was characteristic that a small amount of 2-phenyl isomer and a large amount of 5-phenyl isomer were obtained.

Comparison of Isomer Distribution of Phenylalkan-1-ols with That of Phenylalkanes. The product distributions shown in Tables I, III, and IV seem different from one another even in the equilibrium state, depending on the type of starting hydroxyalkylating agents. Nevertheless, it is interesting to observe ratios of 6 to 7 isomers in various distributions at equilibrium states in which no noticeable side reaction has yet occurred. The ratios lie between 0.57 and 0.63, except for the results in Table IVB which do not show an equilibrium state yet owing to shorter reaction time. In isomer distribution obtained from a reaction of 2-chlorooctane with benzene by aluminum chloride catalyst at 40 °C (2-phenyloctane, 47; 3-, 30; and 4-, 23%), the ratio of 3- to 2-phenyloctane was 0.64. The ratio might also be calcurated as 0.59 from a result obtained from a reaction of 2-bromooctane catalyzed by aluminum bromide at −15 °C.[11] In the present study, the ratios of 6- to 7-phenyl isomers (0.57–0.63) were almost in agreement with the values observed with phenyloctane isomers. Therefore, it is assumed that the formation of 6- and 7-phenyloctan-1-ols is hardly influenced by the terminal polar group.

In Table V, a remarkably high content of 5-phenyl isomer was observed. The ratio of 3- to 2-phenylhexane at equilibrium distribution can be calculated to be 0.59 from a previous report.[1] Ratios of 4- to 5-phenylhexan-1-ols observed in the distribution shown in Table V (0.35–0.48) seem lower than that of phenylhexanes. This fact again suggests that the terminal electron-withdrawing group reduced the stability of the ionic intermediate at the 4 position and a low content of 4-phenyl isomer resulted in products.[12]

Experimental Section

Synthesis of Starting Materials and Authentic Compounds. Synthetic methods of the starting chloroalkan-1-ols and authentic

phenylalkan-1-ols were already reported[4,5] in detail with analytical data (elemental, ^{1}H NMR, or MS spectrometric analysis) in Japanese. In this section, as for these materials except for compounds newly synthesized, only main synthetic routes for the preparations are outlined. Yields of the authentic compounds were rather low because of repeated purifications in addition to many reaction steps.

2-Chloroalkan-1-ols. 2-Chlorohexan-1-ol was obtained by a reaction of 1,2-epoxyhexane with an equimolar amount of stannic chloride in carbon tetrachloride at 0 °C, followed by repeated distillations not to contain any isomeric chlorohexanol, bp 78 °C (20 mm). 2-Chlorooctan-1-ol was synthesized by a similar method from 1,2-epoxyoctane. The product still contained 3% of 1-chlorooctan-2-ol after repeated distillations, bp 73 °C (2mm). Then, the secondary chlorooctanol was synthesized by a hydrogenation of chloromethyl hexyl ketone[13] (bp 73–74 °C (3 mm)) and confirmed not to be converted under the reaction conditions used to develop the data in Table I.

The Mixture of 4- and 5-Chlorooctan-1-ols. 4-Octen-1-ol (described below) was allowed to react with hydrochloric acid during 3 days at room temperature. The organic layer was washed with water, dried over sodium sulfate, and distilled, bp 113–5 °C (11 mm). This fraction consisted of the two chlorooctanol isomers, which were converted to trimethylsilyl ethers with trimethylchlorosilane and pyridine and analyzed by GC (4 to 5 isomer ratio = 23:77).

4-Octen-1-ol and 7-Octen-1-ol. The former unsaturated alcohol was synthesized in a similar manner as described in the literature,[14] bp 124–6 °C (88 mm) (lit. bp 194.1–4.6 °C). The latter was obtained by reduction[15] of ethyl oct-7-enoate (bp 106 °C (22 mm), (lit.[16] bp 210–2 °C)), which was prepared with the electrosynthetic method as appeared in the literature[16] from the potassium salt of ethyl hydrogen azelate:[17] bp 127 °C (88 mm); ^{1}H NMR δ 4.7–5.9 (m, 3, CH=CH₂), 4.43 (s, 1, OH), 3.50 (t, 2, –CH₂O–), 2.0 (m, 2, –CH₂CH=), 0.8–1.7 (m, 8, –CH₂–).

2-Phenylhexan-1-ol and 2-Phenyloctan-1-ol.[4] Both compounds were prepared by the reactions of 1,2-epoxyhexane and 1,2-epoxyoctane with benzene in the presence of an equimolar amount of aluminum chloride at 0 °C, bp 107–8 °C (4 mm) and 112–4 °C (0.8 mm), respectively.

3-Phenylhexan-1-ol and 3-Phenyloctan-1-ol.[5] *n*-Propyl phenyl ketone was hydrogenated with lithium aluminum hydride to 1-phenyl-1-butanol. This was converted to a Grignard reagent (bromide) in ether, followed by a reaction with ethylene oxide to yield 3-phenylhexan-1-ol, bp 80 °C (2 mm). 3-Phenyloctan-1-ol was synthesized in a similar manner using *n*-amyl phenyl ketone as a starting material, bp 133–5 °C (2 mm).

4-Phenylhexan-1-ol and 4-Phenyloctan-1-ol.[5] 2-Phenylbutan-1-ol was prepared from the reaction of 1,2-epoxybutane and benzene with aluminum chloride and converted to a Grignard reagent, which was allowed to react with ethylene oxide to yield 4-phenylhexan-1-ol, bp 100 °C (6 mm). 2-Phenylhexan-1-ol was converted to 4-phenyloctan-1-ol via Grignard reaction with ethylene oxide, bp 132–3 °C (2 mm).

5-Phenyloctan-1-ol.[5] 1,4-Dibromobutane was converted to a Grignard reagent in dibutyl ether and was allowed to react with 1-phenyl-1-bromobutane. Air was bubbled into the reaction mixture to yield 5-phenyloctan-1-ol. This product was contaminated with a hydrocarbon and purified over alumina column.

Friedel–Crafts Reactions and Analytical Methods. To a 50-mL flask equipped with usual apparatus for Friedel–Crafts reaction were charged benzene (0.40 mol) and aluminum chloride (0.03 mol, commercial special grade), which was well pulverized under a dry nitrogen stream. The mixture was kept at 5 °C, to which a hydroxyalkylating agent (0.02 mol) was dropped at the fixed temperature within 1–3 min. The reaction time was measured immediately after dropping. In experiments at higher temperature, the content was warmed to a prescribed temperature as rapidly as possible immediately after addition of the reagent at 5 °C. A sample (0.5 mL) was withdrawn from the reaction mixture by a pipet equipped to the flask at a prescribed time and was poured into a small test tube containing 5% hydrochloric acid (1 mL) and benzene solution (0.5 mL) of an internal standard compound for GC analysis (methyl *n*-octyl ether for phenylhexan-1-ols and 2-phenylhexan-1-ol for phenyloctan-1-ols). A part of the benzene layer was subjected to analysis of remaining hydroxylating agent by GC (column 1). The other part (50 μL) was dried over sodium sulfate and treated with trimethylchlorosilane (100 μL) and pyridine (100 μL) in a sealed tube during 2 h at room temperature. The resulting trimethylsilyl ethers of the phenylalkanols were analyzed by GC (column 2). Column 1: polyethylene glycol 20 M, 20%, 3 m, temperature 190 °C. Column 2: Apiezon Grease L, 20%, 3 m, programmed temperature 180–220 °C at 5 °C/min. Errors of the analysis were presumed to remain less than ±1.5% from a consideration of analytical result using known authentic mixtures. *x*-Phenyloctan-1-ols (*x* = 2–5) and *x*′-phenylhexan-1-ols (*x*′ = 2–4) were identified by GC in the form of trimethylsilyl ethers with authentic samples. Ether derivatives of 6- and 7-phenyloctan-1-ol and 5-phenylhexan-1-ol were isolated by preparative GC, respectively, and identified by ^{1}HNMR and MS.[5] Reaction of 2-chlorooctane with benzene catalyzed by aluminum chloride (0.05 mol) was carried out in a similar manner as that mentioned above. The starting chloride was completely converted within 1 h. Distributions of phenyloctane isomers were determined by GC using column 1.

Transalkylation of a Mixture of *x*-Phenyloctan-1-ols. A mixture of *x*-phenyloctan-1-ols (0.01 mol, obtained by the reaction shown in Table I) was stirred in toluene (0.20 mol) in the presence of aluminum chloride (0.015 mol). Consumed amounts and changes of the composition of *x*-phenyloctan-1-ols after various reaction periods were measured by GC. After the reaction, a mixture of tolyloctanols was separated by vacuum distillation. Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.90; H, 11.23. Detailed analysis on composition of tolyloctanol isomers was not carried out.

Registry No.—1,2-Epoxyhexane, 1436-34-6; 4-chlorooctan-1-ol, 67700-24-7; 5-chlorooctan-1-ol, 67700-25-8; 4-octen-1-ol, 67700-26-9; 7-octen-1-ol, 13175-44-5; potassium ethyl azelate, 67700-27-0; ethyl oct-7-enoate, 35194-38-8; 1,2-epoxyoctane, 2984-50-1; 4-chloro-1-octanol trimethylsilyl ether, 67700-28-1; 5-chloro-1-octanol trimethylsilyl ether, 67700-29-2; propyl phenyl ketone, 495-40-9; 1-phenyl-1-butanol, 614-14-2; 1-phenyl-1-bromobutane, 53118-87-9; ethylene oxide, 75-21-8; amyl phenyl ketone, 942-92-7; 1,2-epoxybutane, 106-88-7.

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