

REACTION PRODUCTS OF FUNCTIONALLY SUBSTITUTED 2-CHLOROPROPANES
WITH BENZENE CATALYZED BY ALUMINUM CHLORIDE

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Reactions of 1-X-2-chloropropanes (X=CH₃O-, HO- and CH₃OCO-) with benzene catalyzed by AlCl₃ have been studied. The former two secondary chlorides gave unusual products, *n*-propylbenzene and 1,1-diphenyl-1-propene, in addition to 1-X-2-phenylpropane, 1,1- and 1,2-diphenylpropanes, respectively, whereas the other one afforded only methyl 3-phenylbutanoate.

In Friedel-Crafts alkylation of benzene with di- or polychloroalkane which contains both primary and secondary chlorides, it has been recognized that the secondary chloride reacts preferentially to the primary one^{1,2)}. The ease of the reaction of secondary chlorides was also observed in alkylation with functionally 1-substituted chloroalkanes, such as 2-chloro-1-octanol³⁾ or 3-chloro-1-butanol⁴⁾, in which the hydroxyl group did not substantially react even in the presence of an excess amount of aluminum chloride.

During the course of a study on the Friedel-Crafts alkylation with functionally 1-substituted chloroalkanes, we found that 1-X-2-chloropropanes (X=CH₃O- (1) and HO- (2)) afforded *n*-propylbenzene (3) which was an unexpected product by the alkylation with secondary chlorides, in addition to 1-X-2-phenylpropane (X=CH₃O (4) and HO- (4')), 1,1-diphenylpropane (5), and 1,2-diphenylpropane (6). 1,1-Diphenyl-1-propene (7) was also detected as an unusual product of the reaction. Ransley reported^{2b)} that a formation of cumene besides (5) and (6) in the reaction of 1,2-dichloropropane. It seemed very remarkable that (3) was formed instead of cumene in the reaction of secondary alkyl chloride derivatives in this work.

The reactions were carried out with 1-X-2-chloropropanes (0.015 mol), benzene

(0.3 mol) and anhydrous aluminum chloride (0.0225 mol, well pulverized under a dry nitrogen atmosphere) at 40°C, and the products were isolated by distillation or by preparative glpc and identified by spectral analyses.

Yields of the reaction products from (1) at various reaction periods are shown in Table 1. The product (4)⁵⁾ initially formed increased till 120 min, then decreased gradually, while (3)⁶⁾ and a mixture of (5) and (6) increased successively. 1,1-Diphenyl-1-propene (7)⁷⁾ began to be detected after 95 min. The conversion at 180 min stage was about 50%⁸⁾. Products (5) and (6) were not satisfactorily separated from each other by glpc (column PEG 6000, 6m), but (6) was found to be the major component by GC-MS analysis⁹⁾. The products (3)–(7) were also obtained by the reaction at 3°C (Yields: (3), 3%; and (4), 7% after 90 hrs).

Table 1. Yields of the products obtained by the reaction of (1)

Time (min)	Yield (% based on the starting chloride)			
	(3)	(4)	(5)+(6)	(7)
45	-	1	1	-
95	1	10	7	1
120	4	11	11	2
150	6	8	17	5
180	7	5	19	5

A similar pattern of the product distribution was observed in reaction of (2) as shown in Table 2, suggesting that (3) was also formed from (2).

Table 2. Yields of the products obtained by the reaction of (2)

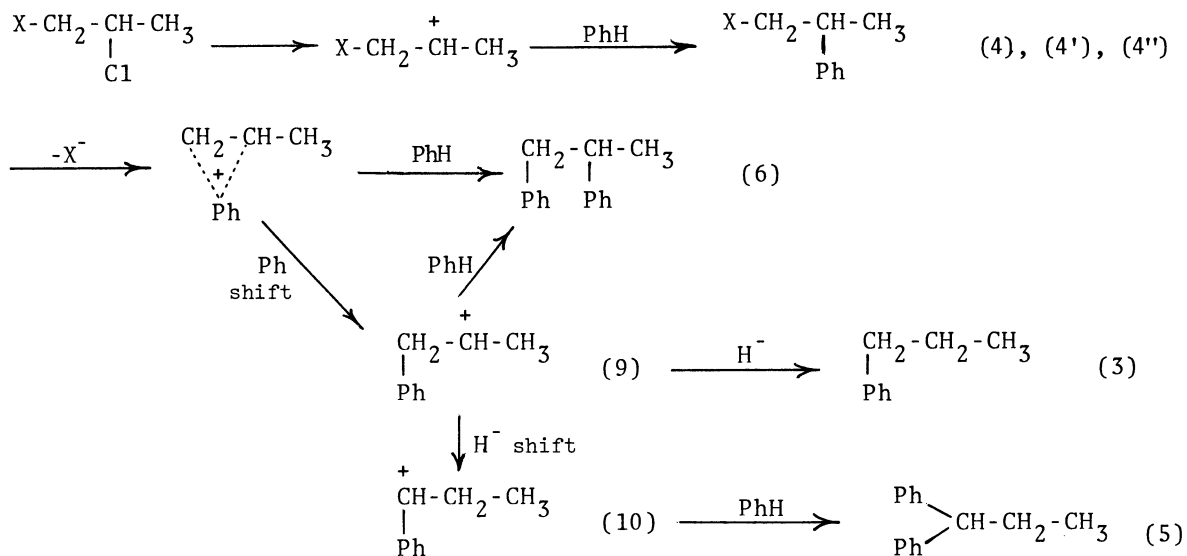
Time (min)	Conver- sion (%)	Yields (% based on the starting chloride)			
		(3)	(4') ¹⁰⁾	(5)+(6)	(7)
20	2	-	2	-	-
90	66	7	24	25	5
130	81	10	7	38	4
180	87	12	3	41	1

Table 3. Yields of (4'') in the reaction of (8)

Time (min)	Conver- sion (%)	Yield (%)
20	12	8
45	67	56
95	99	73
150	100	77
180	-	76

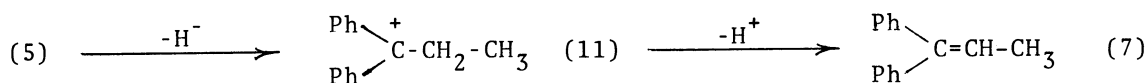
In a similar reaction with methyl 3-chlorobutanoate ($X=CH_3OCO-$, (8)), the ester was completely consumed after 150 min affording only methyl 3-phenylbutanoate (4'')¹¹⁾ as a sole distillable product, and no other by-product was obtained (Table 3).

Over-all reaction process was presumed as shown in the following scheme.



Ransley described a similar scheme for the reaction of 1,2-dichloropropane^{2b)}, but initially alkylated product, 1-chloro-2-phenylpropane which corresponded to (4), (4'), or (4''), was seemed not to be detected in his experiments. The substituents in our study do not ionize so readily as chlorine even in an existence of a very favorable $\text{Ar}_1\text{-3}$ participation¹²⁾ of the adjacent phenyl group causing substantial formations of (4), (4'), and (4''). The less ionizable property of X was remarkably revealed in the reaction of (8), where no other isolable product than (4'') was afforded. *n*-Propylbenzene was seemed to be formed as shown in the scheme. The formation of cumene was reported in the reaction of 1,2-dichloropropane, although the mechanism of its occurrence was not described in the literature^{2b)}. The formation of (3) was considered to support strongly an existence of $\text{Ar}_1\text{-3}$ participation to give a secondary cation (9). Previously, we reported that 1-phenyloctane was obtained as a by-product of a reaction between 1,2-epoxyoctane and benzene catalyzed by an excess of aluminum chloride³⁾. This hydrocarbon is now considered to be formed from 2-chloro-1-octanol which was produced as an intermediate of the reaction between 1,2-epoxyoctane and aluminum chloride.

An unusual product (7) was presumed to be formed from (5) via a resonance stabilized intermediate (11) as shown in the following scheme¹³⁾. This process may coupled with the reaction (9)→(3), and play a role as hydride source in the reaction.



References and Notes

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- 5) The products (4) — (7) were isolated by a preparative glpc.
Analytical data of (4): NMR(CDCl₃, 60 MHz), δ 7.2(m, 5, Ph), 3.3(d, 2, CH₂), 3.27(s, 3, CH₃O), 2.9(m, 1, CH), 1.26(d, 3, CH₃); MS m/e, 150(M⁺).
- 6) NMR(CDCl₃, 60 MHz), δ 7.17(m, 5, Ph), 2.6(t, 2, PhCH₂), 1.6(m, 2, CH₂), 0.95(t, 3, CH₃); MS m/e, 120(M⁺). Found: C, 89.96; H, 10.36%. Calcd for C₉H₁₂: C, 89.94; H, 10.06%.
- 7) NMR(CCl₄, 100 MHz), δ 7.07(m, 10, Ph), 6.03(q, 1, C=CH), 1.74(d, 3, CH₃, J=7.4 Hz); MS m/e, 194(M⁺).
- 8) Accurate conversion could not be estimated because unconverted (1) was not well separated from benzene in glpc.
- 9) High abundance of (6) is in agreement with result observed in the reaction of 1,2-dichloropropane^{2b}).
- 10) The product (4') was identified by glpc using authentic sample which was synthesized by a reaction of propylene oxide with benzene catalyzed by AlCl₃ at 5°C. bp 101.5—103.5°C/6mmHg. NMR(neat, 60 MHz), δ 7.1(m, 5, Ph), 4.59(s, 1, OH), 3.50(d, 2, CH₂), 2.8(m, 1, CH), 1.21(d, 3, CH₃); MS m/e, 136(M⁺).
- 11) bp 81—83°C/4mmHg. NMR(neat, 60 MHz), δ 7.1(m, 5, Ph), 3.42(s, 3, CH₃O), 3.13(m, 1, CH), 2.49(d, 2, CH₂), 1.23(d, 3, CH₃).
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