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Friedel-Crafts Reactions of Benzene with 1-Phenylpropanols. Effects of $CuCl_2$, Cu_2Cl_2, and Decalin

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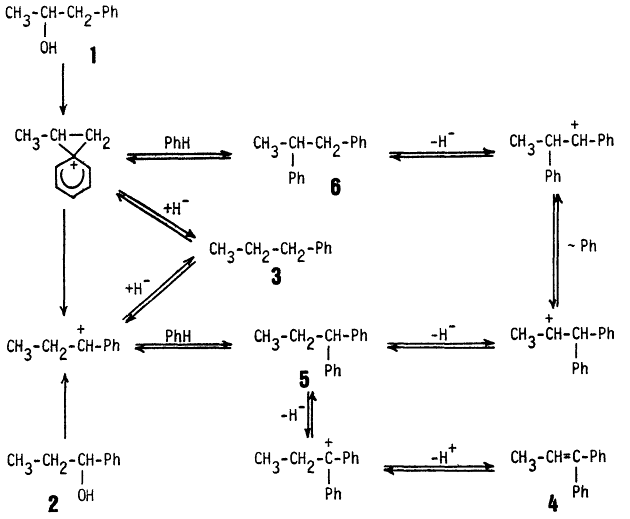
Synopsis. Highly regioselective formation of 1,1-diphenylpropane was observed when copper(I) or (II) chlorides was added to the aluminium chloride-catalyzed reaction of benzene with 1-phenyl-1-propanol. In the reaction with 1-phenyl-2-propanol, the addition of copper salts increased the formation of 1,1-diphenylpropane. The addition of decalin diminished the alkylation reaction to give a reduction product.

In a previous paper, we reported that the Friedel-Crafts reaction of benzene with 2-phenyl-1-propanol, 1-phenyl-2-propanol (**1**), and the related compounds gave a mixture of 1-phenylpropane (**3**), 1,1-diphenylpropene (**4**), 1,1- (**5**) and 1,2-diphenylpropanes (**6**), and we also pointed out that the intermolecular hydride transfer from **5** to an intermediate, 1-methyl-2-phenylethyl or 1-phenylpropyl cation, played an important role in the reaction.1) Schmerling and Vesely reported that an aromatic hydrocarbon was alkylated with a saturated hydrocarbon when it was treated with copper(II) and aluminium chlorides.2) They suggested that the alkylation proceeded by an oxidative reaction involving copper(II) chloride. In order to investigate the effects of oxidizing reagents and hydride donors on the reaction, the aluminium chloride-catalyzed reactions of benzene with 1-phenyl-2- (**1**) and 1-propanols (**2**) were studied in the presence of copper(II) and (I) chlorides, and *trans*-decalin.



Scheme 1.

By the addition of copper(II) chloride as an oxidizing reagent, the yield of 1-phenylpropane (**3**) was diminished as expected, but the yield of 1,1-diphenylpropene (**4**) (an oxidized product) did not increase either in the case of **1** or of **2**. Furthermore, no distinct difference could be observed between the result obtained by the addition of copper(II) chloride and that by copper(I) chloride, in spite of the difference of their oxidizing ability. When the reaction of benzene with **2** was carried out in the presence of the copper salts, the yields of diphenylpropanes remarkably increased and the reaction regioselectively proceeded to afford 1,1-diphenylpropane (**5**). In the reaction with **1**, the addition of the copper salts also increased the yield of diphenylpropanes as well as the ratio of **5** in diphenylpropanes. In the reactions using copper(I) chloride, no distinct difference was observed between the results obtained under the ambient atmosphere and under argon. Nenitzescu and Cantuniari showed that the aluminium chloride-catalyzed hydride transfer reaction took place if the aluminium chloride contained water.3) In the present case, the reaction mixture should contain water since the substrates were alcohols; thus hydride transfer was expected to occur. The present results, however, indicate that both copper(II) and (I) chlorides prevent the intermolecular hydride transfer reaction. Although the reason why the presence of each chloride gave similar results is still uncertain, it is suggested that the copper salts prevent the rearrangement of 1-phenylpropyl cation to a phenonium-type 1-methyl-2-

Table 1. Reaction of benzene with 1-phenylpropanols in the presence of additives

Substrate	Additive	Yield/%a)			5 :	6b)
		3	4	5+6		
$PhCH_2\underset{OH}{\underset{\mid}{C}}HCH_3$ **1**	$CuCl_2$	2	0	85	21	79
	Cu_2Cl_2	0.5	0	75	19	81
	Decalin	80	0	trace	—	—
	None	9	3	67	7	93
$Ph\underset{OH}{\underset{\mid}{C}}HCH_2CH_3$ **2**	$CuCl_2$	3	0	97	100	0
	Cu_2Cl_2	1	0	99	100	0
	Decalin	62	0	trace	—	—
	None	17	4	79	54	46

a) Determined by GLPC. b) Determined by NMR.

phenylethyl cation; the rearrangement probably takes place *via* **5** and **6**, accompanied with hydride transfer and phenyl migration.

The addition of *trans*-decalin increased the yield of the reduction product (**3**), and gave a trace of the Friedel-Crafts alkylation products (**5** and **6**). It is thus indicated that the arylpropyl cations abstract a hydride ion from decalin easier than from **5** and other products, *i.e.*, decalin is very reactive as a hydride donor.

Experimental

The ^{1}H NMR spectra were taken on a JEOL PMX-60 (60 MHz) or a Varian HR-220 (220 MHz) apparatus in $CDCl_3$ with TMS as an internal standard.

Materials. Benzene was washed with conc H_2SO_4, and distilled over CaH_2. Commercial GR grade aluminium chloride was used without further purification. GR grade $CuCl_2$ was used after drying at 120 °C/3 mmHg (1 mmHg ≈133.322 Pa) for more than 3 h. White crystalline Cu_2Cl_2 was prepared from $CuCl_2$ and glycerol, washed with ethanol and dried under a reduced pressure.[4] **1**, **2** and *trans*-decalin were commercially available, and used without further purification.

*The Reactions of Benzene with 1-Phenyl-*1- *and 2-propanols. A Typical Procedure*: A solution of **2** (12 mmol) in benzene (10 ml) was added to a stirred mixture of $AlCl_3$ (22.5 mmol) and the additive ($CuCl_2$, 22.5 mmol) in benzene (20 ml) at 40 °C. The mixture was stirred at 40 °C for 2 h, and then poured into a mixture of saturated aqueous NH_4Cl solution (100 ml) and 30% aqueous ammonia (20 ml). *p*-Methoxytoluene was added as an internal standard, the organic layer was separated, the aqueous layer was extracted with ether, and the combined extracts were dried over $MgSO_4$. After removal of the solvents, the crude product was submitted to the GLPC analysis (PEG-20M 5% on Chromosorb W, 4 m). The crude product was distilled under a reduced pressure, and the diphenyl fraction (bp 109—111 °C/3 mmHg) was analyzed by means of the integral intensities of terminal methyl signals in its NMR spectrum: 1,1-diphenylpropane (**5**), $\delta=0.87$ (t, $J=8$, 3H, CH_3), 2.04 (m, 2H, CH_2), 3.71 (t, $J=10$, 1H, CH), 7.13 (s, 10H, C_6H_5); 1,2-diphenylpropane (**6**), $\delta=1.20$ (d, $J=8$, 3H, CH_3), 2.86 (m, 3H, $-CH_2-CH\langle$), 7.15 (10H, C_6H_5); 1,1-diphenylpropene (**4**), $\delta=1.73$ (d, $J=8$, 3H, CH_3), 6.15 (q, 1H, $=CH-$), 7.19 (s, 10H, C_6H_5).

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