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REACTIVITIES OF ALLYLCHLORIDES IN THE FRIEDEL-CRAFTS REACTION CATALYZED BY TUNGSTEN HEXACHLORIDE

Isao MOCHIDA*, Kenjiro TAKESHITA*, Michiharu OHGAI
Takao TANAKA, and Tetsuro SEIYAMA
Research Institute of Industrial Science*, and
Department of Applied Chemistry, Faculty of Engineering,
Kyushu University, Fukuoka, 812

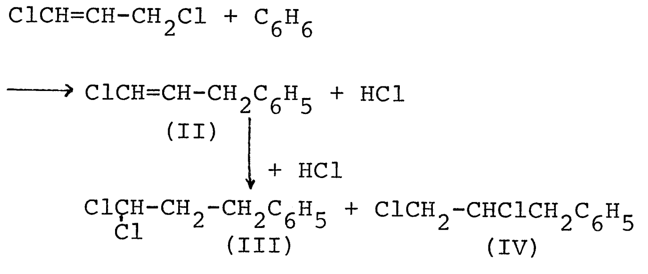
The reactivities of substituted allyl chlorides have been studied in the alkylation reaction catalyzed by WCl_6. The primary products were allyl benzenes, however, they suffered consecutive hydrochlorination to the extent, which depended on their structure. The reactivity order of the allyl chlorides was trans-$CH_3CH{=}CHCH_2Cl > CH_2{=}CHCH_2Cl >$ trans-$ClCH{=}CHCH_2Cl >$ cis-$ClCH{=}CHCH_2Cl$. This order may be explained in terms of electronic effects of substituent groups in the polarized-complex intermediates.

Although the alkylation reaction of allylic compounds seems to be an expedient way to obtain allylbenzenes in a high selectivity, such trials have been scarcely successful.[1, 2] Tungsten hexachloride has been found to catalyze such an alkylation of 1,3-dichrolopropene in a high yield by the present authors. The reactivities of four allylic compounds in the reaction were studied to discuss the electronic and steric effects of the substituent groups. Based on the product structure, the reactivity order of our study, and accumulated knowledge in Friedel-Crafts reactions,[2] the reaction mechanism was also discussed.

Alkylating agents of allyl chloride, trans/cis-1,3-dichloropropene (mixture; trans/cis = 1.2), and trans-crotyl chloride obtained from Tokyo Kasei Co., were dried and distilled under nitrogen. Tungsten hexachloride (Ishizu Seiyaku Co.) was purified by the sublimation. The alkylation reaction was carried out in a sealed glass tube which contained 0.2 ml allyl compound, 10 ml benzene, and 16 mg WCl_6. Reaction products were identified by gas chromatography, MNR, and Mass spectroscopy.

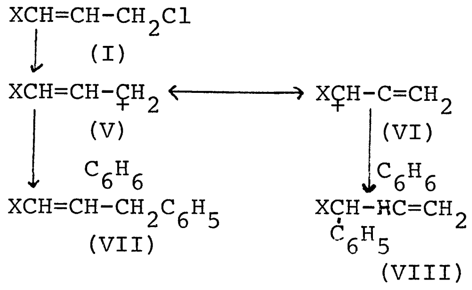
Trans/cis-$ClCH{=}CHCH_2Ph$, $CHCl_2CH_2CH_2Ph$ and $CH_2ClCH_2CHClPh$ were found in the products from the reaction of trans/cis-1,3-dichloropropene. From trans-crotylchloride, trans-$CH_3CH{=}CHCH_2Ph$, $CH_3CH_2CHClCH_2Ph$ and $CH_3CHClCH_2CH_2Ph$ were identified. Substitution at the double bond might give $PhCH{=}CHCH_2Cl$, so that such an alkylation is ruled out, indicating an exclusive alkylation at the allylic position.

Products identified indicate that the alkylation was followed by hydrochlorination. The reaction profile in Fig. 1 clearly shows the consecutive hydrochlorination of 1-chloro-3-phenyl-propene-1(II) (Scheme 1), which preferred the formation of III to IV. The polarized complex and the carbonium ion have been proposed as the



$$\begin{array}{l}ClCH=CH-CH_2Cl + C_6H_6 \\ \longrightarrow ClCH=CH-CH_2C_6H_5 + HCl \\ \qquad (II) \downarrow + HCl \\ \underset{Cl}{ClCH}-CH_2-CH_2C_6H_5 + ClCH_2-CHClCH_2C_6H_5 \\ \qquad (III) \qquad\qquad\qquad (IV)\end{array}$$

Scheme 1



$$\begin{tikzcd} XCH=CH-CH_2Cl \arrow[d, "(I)"] & \\ XCH=CH-\overset{+}{C}H_2 \arrow[r, leftrightarrow] \arrow[d, "C_6H_6"', "(V)"] & X\overset{+}{C}H-C=CH_2 \arrow[d, "C_6H_6"', "(VI)"] \\ XCH=CH-CH_2C_6H_5 \ (VII) & \underset{C_6H_5}{XCH}-HC=CH_2 \ (VIII) \end{tikzcd}$$

Scheme 2

intermediates for the alkylation reaction.[2, 3] The carbonium ion, V, produced from the allylic compound(I) might easily isomerize into VI, which is more stable than V(Scheme 2). However, VIII could not be found in the products of any allylic reagent in the present study, denying the equilibrium of carbonium ions.

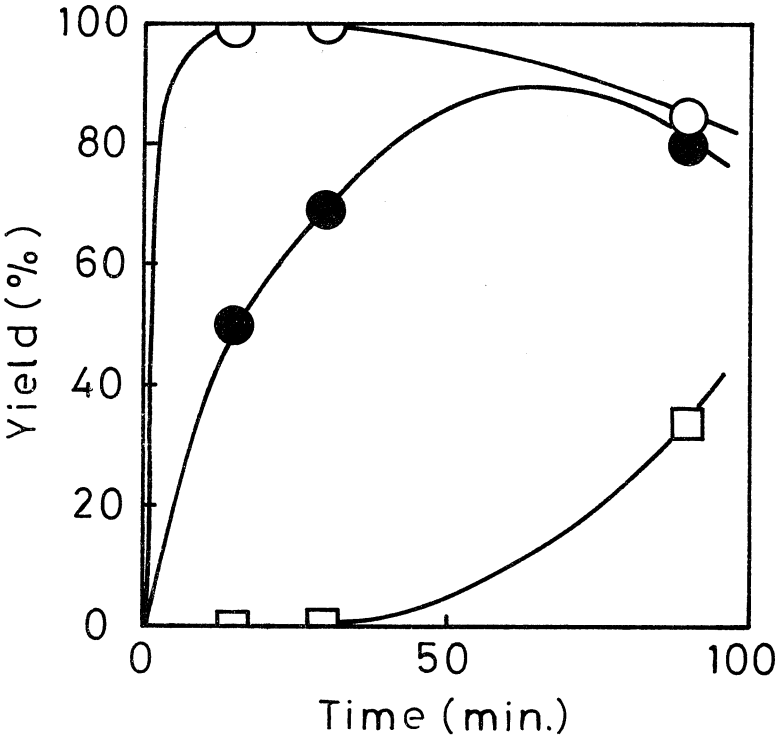


Fig. 1. The Reaction of trans/cis-1,3-dichloropropene(trans/cis = 1.2) with Benzene.

Reaction conditions; propene/WCl_6 = 22

benzene/propene = 5

25°C

○ : trans-$phCH_2CH=CHCl$

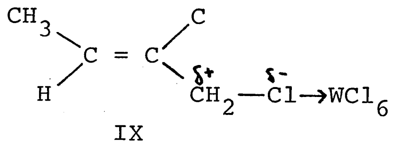
● : cis-$phCH_2CH=CHCl$

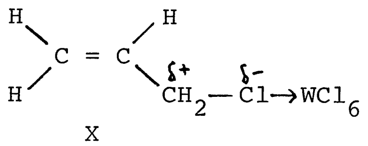
□ : $phCH_2CH_2CHCl_2 + phCH_2CHClCH_2Cl$

Figure 1 indicates higher reactivity of the trans form of 1,3-dichloropropene than that of the cis form. Alkylation reactivities of allylic reagents are summarized in Table 1. This kind of alkylation is usually considered to proceed via a S_N2 mechanism,[3] however the same compounds were reported to show a quite different reactivity order in the Finkelstein reaction, which has been also considered as a S_N2 reaction.[4] The difference may be explained as following; The major role of resonance effect of the substituents may have methyl and chlorine groups to give similar contribution to the reactivity of allyl chloride for the Finkelstein reaction. In contrast, the inductive effect of substituents may play an important role in the alkylation reactions. The role of the double bond should be also taken into account for the stabilization of the cationic intermediate as shown by the fact that 1,3-dichloropropane did not react at all in the present condition in spite of the similar inductive effect of chlorine. The interaction of WCl_6 with the olefinic double bond is also possible to have effects on the reactivity.[6]

Table 2.
The reactivity of allyl compounds in the alkylation and Finkelstein reaction[4]

	Relative Reactivity		σ * value[5] of XCH =CH- group
Reaction	$RCl+C_6H_6$	RCl+KI[4]	
Temp. [°C] Reagent	0	20	
trans-CH_3-CH=CH-CH_2Cl	9.7	1.56	0.360
CH_2=CH-CH_2Cl	1.0	1.00	0.653
trans-Cl-CH=CH-CH_2Cl	0.3	2.90	0.900
cis-Cl-CH=CH-CH_2Cl	0.03	8.58	—
Cl-CH_2-CH_2-CH_2Cl	no react	-	0.385


IX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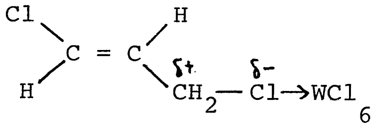
XI

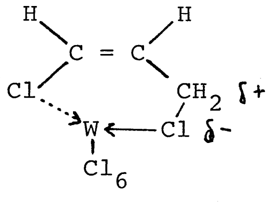
XII

Fig. 2. Assumed Intermediates.

Because the catalyst of WCl_6 should join in the polarized-complex intermediate of alkylation reaction, the intermediates as shown in Fig. 2 can be assumed. The reactivities of the first three(IX > X > XI) in Table 2 can be explained in terms of the inductive effects of the γ-substituents, which can be described by σ^* values of XCH=CH-. The electron-releasing group accelerated the reaction rate, perhaps because it may stabilize the positive polarization of the allylic carbon, favoring the formation equilibrium of the intermediate. However, an additional factor due to the simultaneous interaction of WCl_6 with γ-chlorine in the cis position may be also taken into account for the lowest reactivity of XII. This interaction should decrease the polarization of allyl carbon-chlorine bond.

The reactivity of the consecutive hydrochlorination depended also on the structure of allyl benzenes produced. Allylbenzenes without chlorine substituent suffered such a rapid hydrochlorination that the yields of 3-phenyl-propene-1 and trans-crotylbenzene were less than 20 % even in 5 minutes reaction at 0°. In contrast, the consecutive reaction of 1-chloro-3-phenyl-propene-1(II) was much slower than the alkylation, leading to a high yield of II as shown in Fig. 1. To surpress the consecutive hydrochlorination of reactive allylbenzenes, hydrogen chloride produced should be removed from the reaction system.

Consecutive hydrochlorination of trans/cis-$phCH_2CH{=}CHCl$ and trans-$phCH_2CH{=}CHCH_3$ gave $phCH_2CHClCH_2Cl$(18 %), $phCH_2CH_2CHCl_2$(82 %) and $phCH_2CHClCH_2CH_3$(46 %) $phCH_2CH_2$-$CHClCH_3$(54 %), respectively(Numbers in parentheses indicate the selectivities.). Such orientation of addition may be explained by the stability of carbonium ions.[7,8]

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