

Direct Allylation of Aromatic Compounds with Allylic Chloride using the Supported Reagents System $\text{ZnCl}_2/\text{SiO}_2\text{-K}_2\text{CO}_3/\text{Al}_2\text{O}_3$

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Although the reaction of aromatic compounds with allylic chlorides using $\text{ZnCl}_2/\text{SiO}_2$ gives 2-chloro-1-arylalkanes accompanied with diarylalkanes, similar reaction using $\text{ZnCl}_2/\text{SiO}_2\text{-K}_2\text{CO}_3/\text{Al}_2\text{O}_3$ produces the monoallylated compound as the major product in good yield.

Direct allylation of aromatic compounds by electrophilic aromatic substitution reaction is usually very difficult. Recently, the use of allylmetal compounds and metal complexes for direct allylation of aromatic compounds has been reported.¹ Friedel-Crafts allylation of aromatic compounds using allyl chloride or allyl alcohol and an acid catalyst has been shown to give a complex mixture, apparently resulting from further reaction of the initial products, and the yield of allylation product is very low,² and so it has not been developed as a synthetic method. Reaction of benzene with allyl chloride using FeCl_3 has been reported to give 2-chloro-1-phenylpropane **2** and 1,2-diphenylpropane **4** as a by-product, which is evidently formed by further reaction of **2** with benzene.³ Compound **2** is formed by addition of hydrogen chloride to the double bond of allylbenzene **1** initially formed. Thus it should be possible to obtain **1** selectively from a Friedel-Crafts reaction with allyl chloride if the hydrogen chloride can be removed as fast as it is formed. Recently montmorillonite-supported zinc chloride has been reported to be an extremely effective Friedel-Crafts alkylation catalyst, whereas unsupported zinc chloride is one of the weakest Friedel-Crafts catalysts.⁴ Here we describe the direct allylation of aromatic compounds with allyl chloride using the supported reagents system consisting of silica gel-supported ZnCl_2 as an acid catalyst and alumina-supported K_2CO_3 as a scavenger of hydrogen chloride.

Allyl chloride reacted with benzene in the presence of AlCl_3 at 30 °C for 1 h to give a mixture of **3** and **4** as the major products, and the yield of **1** was <10%, whereas the similar reaction using $\text{ZnCl}_2/\text{SiO}_2$ gave **2** as the major product. Allylbenzene **1** should be selectively obtained by carrying out the reaction using $\text{ZnCl}_2/\text{SiO}_2$ in the presence of a base to remove hydrogen chloride. However, a combination of $\text{ZnCl}_2/\text{SiO}_2$ and an amine such as *N,N*-dimethylaniline cannot be used because ZnCl_2 is strongly complexed with amines. The reaction using K_2CO_3 as a solid base instead of an amine did not proceed to a significant extent, and K_2CO_3 deactivated the catalyst, ZnCl_2 . In contrast, when alumina-supported K_2CO_3 was used as solid base, **1** was obtained in 70% yield (see Table 1). These results suggest that contact between ZnCl_2 and K_2CO_3 , which are supported on silica gel and alumina respectively, is difficult because they are located mainly in holes of the porous solids. This method is applicable to various kinds of aromatic compounds and allylic chlorides. As can be seen in Table 2, allylation of aromatic hydrocarbons with allylic chlorides at 30 °C using the supported reagents system which involves co-


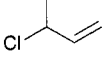
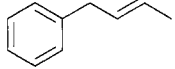

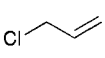
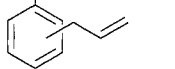

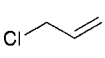
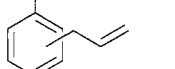

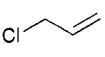
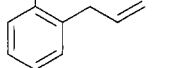

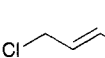
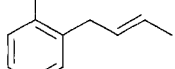


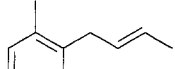
suspension of $\text{ZnCl}_2/\text{SiO}_2$ and $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$ in an organic solvent gave the corresponding allylated compounds in good yields. Reaction of *p*-xylene with crotyl chloride or 3-chlorobut-1-ene gave the same allylic derivative. Chlorobenzene also reacted with allyl chloride at 50 °C for 24 h to give a mixture of

Table 1 Reaction of benzene with allyl chloride in the presence of acid and base^a

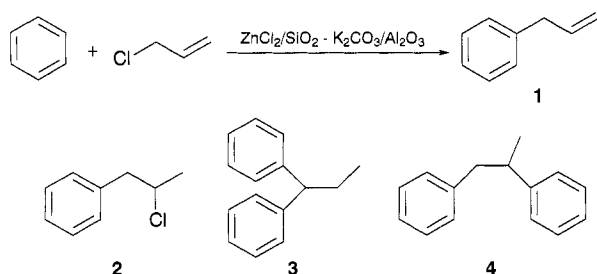
Acid	Base	Yield of products (%) ^b		
		1	2	3 + 4
AlCl_3	—	7	^c	74
$\text{ZnCl}_2/\text{SiO}_2$	—	^c	65	15
$\text{ZnCl}_2/\text{SiO}_2$	Amine ^d	No reaction		
$\text{ZnCl}_2/\text{SiO}_2$	K_2CO_3	5	2	^c
$\text{ZnCl}_2/\text{SiO}_2$	$\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$	70	15	2
—	$\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$	No reaction		

^a Allyl chloride (2 mmol), benzene (5 ml), acid (0.4 mmol), and base (1.45 mmol) at 30 °C for 1 h. ^b The yield based on allyl chloride was determined by GLC. ^c Trace. ^d *N,N*-dimethylaniline.

Table 2 Allylation of aromatic compounds with allylic chlorides in the presence of $\text{ZnCl}_2/\text{SiO}_2\text{-K}_2\text{CO}_3/\text{Al}_2\text{O}_3$ ^a

Aromatic	Allylic chloride	Product	Yield (%) ^b
			61
			78
			77
			73
			76
			81

^a At 30 °C for 1 h. ^b The yield based on allylic chloride was determined by GLC. ^c 50 °C, 24 h.



o- and *p*-chloroallylbenzene in 77% yield. Control experiments carried out in the absence of K_2CO_3/Al_2O_3 gave the corresponding chlorides and diarylalkanes accompanied by trace amounts of allylic products.†

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Footnote

† In a typical experiment, to a solution of allyl chloride (2 mmol) and *p*-xylene (20 mmol) to 1,2-dichloroethane (5 ml) was added $ZnCl_2/SiO_2$ (0.4 g) and K_2CO_3/Al_2O_3 (2.0 g). Silica gel-supported $ZnCl_2$ was prepared as follows. Silica gel (Wakogel C-200, 31.7 g) was added to a solution of zinc chloride (5.0 g) in methanol (80 ml), and the mixture was stirred at room temperature for 0.5 h. The methanol was removed by using a rotary evaporator, and the resulting reagent was then dried *in vacuo* (15 mmHg) at 150 °C for 12 h. Alumina-supported K_2CO_3 was prepared as follows. To a solution of K_2CO_3 (5.0 g) in distilled water (60 ml) was added neutral

alumina (ICN Biomedical N-Super 1, 45 g), and the mixture was stirred at room temperature for 0.5 h. After removal of the water, the resulting reagent was dried *in vacuo* (15 mmHg) at 150 °C for 12 h.

The mixture of allyl chloride, *p*-xylene and supported reagents was stirred vigorously at 30 °C for 1 h. The mixture was filtered, and the solid washed with 1,2-dichloroethane. The filtrate and washings were combined and concentrated, and the products analysed by GLC, MS and NMR spectroscopy.

References

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