

Functional selectivity in Friedel–Crafts alkylations with allylic halides promoted by solid composite lead fluoride reagent

Junko Ichihara*

Institute of Scientific and Industrial Research, Osaka University, Mihogaoka, Ibaraki, Osaka 567, Japan


The composite lead fluoride reagent prepared from PbF_2 and NaBr is a nonhygroscopic and efficient solid reagent for promoting Friedel–Crafts type reaction of aromatic compounds with allylic halides selectively to afford the monoallylated compounds.

Friedel–Crafts type allylation of aromatic compounds using allylic alcohols or halides and Lewis acid catalysts has proved unsatisfactory, because the reaction occurs both at the double bond and at the allylic carbon to yield polyaryl-substituted alkanes.¹ The reactions with allylic halides liberates hydrogen halide, which further attacks the double bond of the products to induce the second reaction. Recently Kodomari *et al.* have reported successful selective monoallylation by using a combination of a solid acid and a solid base, $\text{ZnCl}_2\text{-SiO}_2$ and $\text{K}_2\text{CO}_3\text{-Al}_2\text{O}_3$.² The solid base operates as a scavenger of hydrogen halide liberated during the reaction and does not influence the catalytic activity of the solid Lewis acid because of the distance between both solid supported reagents. Solid acids such as acidic zeolites and clays has been applied to achieve functionally selective allylations with allylic alcohols.^{3,4}

We have studied the use of synergistic interactions between diverse inorganic solid reagents for enhancing solid–liquid heterogeneous reactions with organic compounds dissolved in organic solvents. Recently we have observed that a combination of lead fluoride and a small amount of sodium bromide accelerates the fluorination of allylic and benzylic halides.^{5,6} It was found that a new inorganic lead compound was formed from the solid reagents during the fluorination of organic halides, and that its formation process is associated with activation of the alkyl halides. This prompted us to examine it as a promoter for Friedel–Crafts alkylation reactions. Here we report that the composite lead fluoride reagent is a mild and efficient solid reagent for promotion of selective Friedel–Crafts type monoallylation when used in stoichiometric amounts.⁷

A composite lead fluoride reagent **A** (Pb_3BrF_5) was easily prepared by mixing aqueous NaBr and PbF_2 powder (3 equiv.).†

Table 1 Friedel–Crafts allylation of *p*-xylene and 1-chlorobut-2-ene



Run	Reagent	GC Yield of ArR (%) (t/h) ^a
1	Reagent A (Pb_3BrF_5)	43 (1) 86 (2)
2	Reagent B (Pb_3ClF_5)	27 (1) 80 (2)
3	NaBr-PbF_2	36 (1) 48 (2)
4	PbF_2	0 (1) 0 (2)
5	TiCl_4 (10 mol%) at 3–4 °C	65 (1) ^b
6	$\text{ZnCl}_2\text{-K10}$ (10 mol%)	63 (0.5) ^b

^a 1-Chlorobut-2-ene : *p*-Xylene : Reagent = 1 : ca. 20 : 0.6. ^b By-products were observed by GC.

Using the solid reagent **A**, an electrophilic substitution of *p*-xylene with 1-chlorobut-2-ene proceeded at room temp. to give the corresponding monosubstituted products (**ArR**) in 86% yield after 2 h (Table 1). The composite lead fluoride reagent **B**, prepared from NaCl and PbF_2 , also showed high reactivity. Under the same reaction conditions, PbF_2 showed no reactivity, but a mixture of NaBr and PbF_2 promoted the reaction.

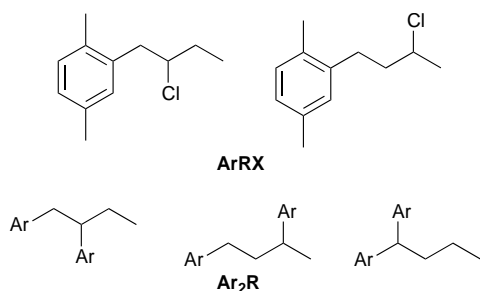
Table 2 Friedel–Crafts allylation using Pb_3BrF_5 solid reagent^a

Allylic Halides	Aromatics	<i>T</i> /°C	t/h	Products	Yield (%)
	Benzene	60	2		94
	<i>p</i> -Xylene	60	2		91
	<i>p</i> -Xylene	60	10		91
	Benzene	room temp.	3		45 ^b
	Toluene	room temp.	2		99 ^{c,d}
	<i>p</i> -Xylene	room temp.	2		77
	Toluene	room temp.	2		85 ^d
	<i>p</i> -Xylene	room temp.	2		77
	<i>p</i> -Xylene	room temp.	48		87 ^c
	<i>p</i> -Xylene	room temp.	2		93 ^c
	<i>p</i> -Xylene	room temp.	1		70 ^{b,c}

^a Alkyl halide : aromatic : Pb_3BrF_5 = 1 : ca. 20 : 0.5. ^b Alkyl halide : aromatic : Pb_3BrF_5 = 1 : 140 : 1. ^c Isolated yields. The others are GC yields. ^d *opm*-isomer ratio = 1 : 1 : 0.1, determined by ¹H NMR spectroscopy.

Accordingly, in the latter case the reagent **A** or **B**, formed in the course of the reaction, was considered to participate in the reaction.

Catalytic activities of TiCl_4 and ZnCl_2 -Montmollironite K-10 (ZnCl_2 -K-10), well-known as mild Lewis acid catalysts, were compared with those of the lead reagents in the reaction.^{8,9}† These catalysts showed higher reactivities but gave considerable amounts of by-products. In the presence of 10 mol% of ZnCl_2 -K-10, a 63% yield of the monoallylated product **ArR** and a 24% yield of its hydrogen chloride adduct (**ArRX**) were formed as major products, with a 2% yield of diaryl substituted alkanes (**Ar₂R**). Kodomari *et al.* have reported that **ArRX**- and **Ar₂R**-type products are mainly formed in the reaction of benzene and allyl chloride with silica-supported ZnCl_2 . On the contrary, in the case of our reagent **A** such by-products were scarcely detected by GC, and the desired product **ArR** was selectively formed and maintained intact in the reaction mixture even after prolonged. Thus, the reagent was found to have functional selectivity, in that it operates on the allylic carbon rather than on the double bond. The selective allylation occurs because the reagent behaves as both the Lewis acidic catalyst and a trap for the liberated halide, *via* exchange with fluoride.



The reaction required at least stoichiometric amounts of the reagent. It was shown by powder X-ray diffraction analysis that the reagent **A** is converted to PbClF during the reaction.

Table 2 shows typical examples for some allylic halides. In all cases the heterogeneous reaction of aromatic compounds and allylic halides using the Pb_3BrF_5 solid reagent proceeded

smoothly under mild reaction conditions and the corresponding monoallylated compounds were obtained in good to excellent yields. The allylation of *p*-xylene by the more reactive 1-chloro-3-methylbut-2-ene was also performed without consecutive cyclization at C–C double bond. Further, our allylation method can be performed under the atmosphere, and requires simple isolation procedures, since the solid reagent is nonhygroscopic and easy to handle.

In conclusion, composite lead fluoride reagents were found to promote Friedel–Crafts allylation selectively and efficiently, thus demonstrating that they are a new and unique type of solid reagent exhibiting mild Lewis acidity and halide capture abilities.

Footnotes and References

* E-mail: ichihara@sanken.osaka-u.ac.jp

† Powder X-ray diffraction analysis of the reagent **A** showed not a mixture of the known lead compounds PbF_2 , PbBrF or PbBr_2 , but the formation of a new lead compound. It was determined by X-ray fluorescence analysis that the reagent was composed of Pb, Br and F in 1.0:0.3:1.8 molar ratio. Therefore, the reagent **A** has the formula Pb_3BrF_5 .

‡ ZnCl_2 -K10 purchased from Fluka was used.

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