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Direct Sulfonylation of Lithiated Alkyl Phosphonates with Benzenesulfonyl Fluoride; Facile Method for Preparation of α-Sulfonyl Alkyl Phosphonates and Vinyl Sulfones

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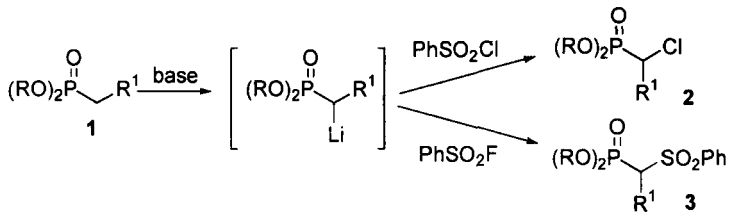
Abstract : α-Sulfonyl phosphonates were synthesized by direct sulfonylation of lithiated alkyl phosphonates with benzenesulfonyl fluoride which have shown different reactivity from benzenesulfonyl chloride, generally known as a sulfonylating reagent.

α-Sulfonyl phosphonates[1] have been proven very useful synthones for synthesis of vinyl sulfones[2], which are widely known as useful intermediates in organic synthesis, and several routes for synthesis of α-sulfonyl phosphonates have been reported such as oxidation of α–phenylthioalkylphosphonates[3], phosphorylation of lithiated alkyl sulfones[4]. But, to our knowledge, no direct sulfonylating reagent in α-position of alkyl phosphonate are known. Previously, we reported that benzenesulfonyl chloride, generally known as a sulfonylating reagent[5], can be used as a chlorenium source for lithiated phosphonates' case[6]. The extension of these

results, we examined the reactivity of benzenesulfonyl fluoride with lithiated alkyl phosphonates and report the benzenesulfonyl fluoride can be used as a direct sulfonylating reagent for alkyl phosphonates (**1**), in contrast to benzenesulfonyl chloride.



Scheme 1

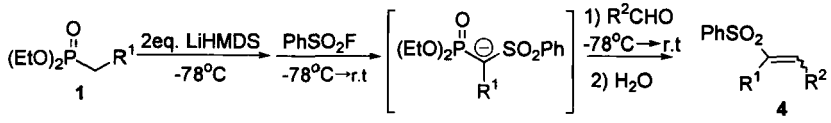
As shown in **Scheme 1**, benzenesulfonyl fluoride acted as a sulfonylating reagent in α-position of lithiated alkyl phosphonate. But yields were varied with the kind and amount of base (**Table 1**).

Table 1. Synthesis of α-Sulfonyl Phosphonates **3**.

Entry	R	R^1	Condition[a]	Yield (%)[b]
a	Ethyl	H	A	45
b	Ethyl	H	B	52
c	Ethyl	H	C	77
d	Ethyl	H	D	76
e	Methyl	H	C	73
f	Isopropyl	H	C	65
g	Ethyl	Me	C	73
h	Ethyl	Ph	C	69

a. Condition A: LDA 1eq. THF -78°C, Condition B: LDA 2eq. THF -78°C, Condition C: Li HMDS 2eq. THF -78°C, Condition D: Li HMDS 3eq. THF -78°C. b. Isolated Yield.

Table 2. Synthesis of Several Vinyl Sulfones.



Entry	R^1	R^2	Yield (%)	mp (°C)
a	H	Ph	64[a]	71.4
b	Me	Ph	63[a]	87.7
c	Ph	Ph	52[a]	181
d	H	*p*-Cl-Ph	75[b]	130
e	H	3-NO_2-Ph	67[b]	143.3

a. Isolated by column chromatography.
b. Isolated by recrystallization.

Typical procedure for synthesis of diethyl phenylsulfonylmethylphosphonate (entry **c** in **Table 1.**) are as follow: To a stirred solution of diethyl methylphosphonate (0.152 g, 1.0 mmole) in dry THF (4 ml) under N_2 and at -78°C, Lithium hexamethyldisilazide (2.2 ml, 2.2 mmole, 1.0 M solution in hexane) was added. After 1 hr., benzenesulfonyl fluoride (0.176 g, 1.1 mmole) in 1 ml of THF was added and the resulting solution allowed to warm to room temperature for 1.5 hr. The clear, colorless (or pale yellow) solution was poured into 5 ml of saturated NH_4Cl, extracted with Et_2O (20 ml x 3), washed with diluted sulfuric acid solution, dried over $MgSO_4$. The solvent was removed under reduced pressure. The residual oil purified by flash column chromatography (EtOAc:Hexane = 1:1) gave the product diethyl phenylsulfonyl-methylphosphonate (0.225 g, 77 %).

In case of using LDA, side products were found which could not be isolated. Yield could be improved when bulky base was used. Li HMDS showed the best result compared with other base. Besides, stoichiometric amount of base could reduce the yields, which might be due to the proton exchange between lithiated alkyl phosphonate and produced α-sulfonyl phosphonate. No better result was shown in the case of 3 eq. of base was used.

Vinyl sulfones **4** could be produced in one-pot from subsequent addition of aldehydes before quenching in the procedure described above (**Table 2**). As known earlier[3], vinyl sulfones were obtained in moderate yield from intermediate **4** in this procedure (E/Z ratio = >99:1 except entry **c** which cannot be determined in NMR).

In conclusion, we report the benzenesulfonyl fluoride as a new, versatile reagent for direct sulfonylation of lithiated alkyl phosphonates. And using above procedure, we obtained the vinyl sulfones in one-pot from alkyl phosphonates.

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