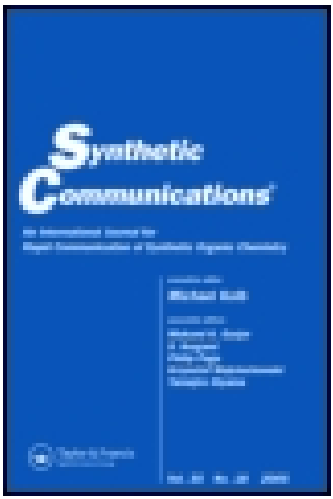

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A Facile Method for the Preparation of 1,1-Dichloroolefins Using Benzenesulfonyl Chloride as a Chlorenium Ion Source

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A FACILE METHOD FOR THE PREPARATION OF 1,1-DICHLOROOLEFINS USING BENZENESULFONYL CHLORIDE AS A CHLORENIUM ION SOURCE.

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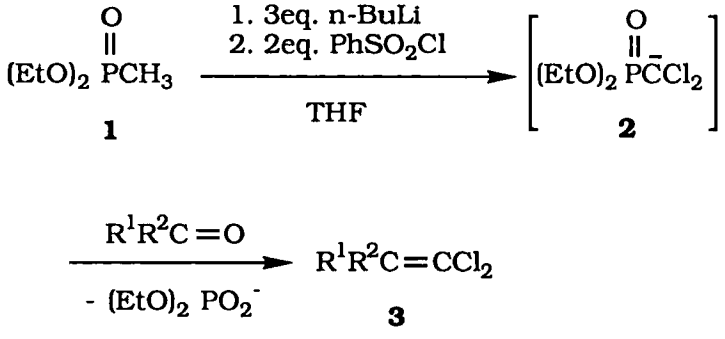
ABSTRACT: Reaction of the lithio anion derived from diethyl methylphosphonate with benzenesulfonyl chloride gives directly the (diethylphosphoryl)dichloromethyllithium. *In situ* reaction with aldehydes or ketones gives in high yields of 1,1-dichloroolefins in a convenient one-pot procedure.

1,1-Dichloroolefins are important synthetic intermediates, especially for the synthesis of arylacetic acids[1] and various alkynes.[2] The commonly used methods for the preparation of 1,1-dichloroolefins are the dichloroolefination of carbon oxygen double bond of carbonyl compounds with Wittig-type reagent obtained from organophosphine and tetrahalomethane and Horner-Emmons reagent generated from cathodic reduction of diethyl trichloromethyl



Scheme

phosphonate.[3] It also has been reported to use of (trimethylsilyl)dichloromethylanion as a Peterson-type reagent.[4] Here we report a modified, one-step synthesis of 1,1-dichloroolefins starting from diethyl methylphosphonate which uses the benzenesulfonyl chloride as a chlorenium ion source[5] and the (diethylphosphoryl)dichloromethyllithium as a key intermediate as shown in Scheme.

(Diethylphosphoryl)dichloromethyllithium(**2**) readily prepared from diethyl methylphosphonate(**1**) and 2 equivalents of benzenesulfonyl chloride in the presence of 3 equivalents of n-BuLi in THF at -78°C, reacts with carbonyl compounds to afford the corresponding 1,1-dichloroolefins(**3**) in good yields. The results are summarized in Table.

The typical experimental procedure is as follows: To a stirred solution of diethyl methylphosphonate(2 mmol) in dry

Table. Synthesis of 1,1-dichloroolefins.

Run	Carbonyls	Products	Yields(%)[a]
1	PhCHO	$PhCH=CCl_2$	82
2	*p*-$MeOC_6H_4CHO$	*p*-$MeOC_6H_4CH=CCl_2$	90
3	*p*-ClC_6H_4CHO	*p*-$ClC_6H_4CH=CCl_2$	90
4	PhC(O)Ph	$Ph_2C=CCl_2$	82[b]
5	$PhC(O)CH_3$	$PhCH_3C=CCl_2$	86
6	 =O	 =CCl_2	66
7	$CH_3(CH_2)_6CHO$	$CH_3(CH_2)_6CH=CCl_2$	75

[a]Isolated yields based on carbonyl compounds.
[b]Crystallized with EtOH, M.P. : 79-80°C

THF(6mL) was added n-BuLi(6 mmol, 1.6 M in hexane) at -78°C under nitrogen atmosphere. After being stirred for 30 min at -78°C, benzensulfonyl chloride(4 mmol) and carbonyl compounds(2 mmol) were added successively and allowed to stand at room temperature for 1h under stirring. Usual aqueous work-up gave the crude products. Pure samples were obtained by SiO_2 column chromatograpy (Et_2O/n-Hexane = 1/4). The reaction of diethyl

methylphosphonate with 2 equivalents of benzenesulfonyl chloride in the presence of 3 equivalents of n-BuLi proceeds rapidly at -78°C for 1 min, yielding the corresponding (diethylphosphoryl)dichloromethyllithium, which is identified by aqueous quenching to give diethyldichloromethylphosphonate in quantitative yield[6]. The present method works well for both aldehydes and ketones as shown in Table. It is of interest to note that the reaction of aldehydes with (diethylphosphoryl)chloromethyllithium gives diethyl 1,2-epoxyalkane phosphonates[7] and no reaction occurs with use of LDA as a base, which is due to the formation of N,N-diisopropyl sulfonamide by the reaction of LDA with benzenesulfonyl chloride.

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