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

Kilsung Lee^a, Won Suk Shin^a & Dong Young Oh^a ^a Department of Chemistry, Korea Advanced Institute of Science and Technology, P.O. Box 150 Cheongyang-Ni, Seoul, 130-650, Korea Published online: 23 Sep 2006.

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

Kilsung Lee, Won Suk Shin, and Dong Young Oh*

Department of Chemistry Korea Advanced Institute of Science and Technology P.O. Box 150 Cheongyang-Ni, Seoul 130-650, Korea

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 acids¹ 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

1657



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 source⁵ 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

Run	Carbonyls	Products	Yields(%) ^a
1	PhCHO	PhCH=CCl ₂	82
.2	p-MeOC ₆ H ₄ CHO	<i>p</i> -MeOC ₆ H ₄ CH=CCl ₂	90
3	p-ClC ₆ H ₄ CHO	p-ClC ₆ H ₄ CH=CCl ₂	90
4	PhC(O)Ph	$Ph_2C=CCl_2$	82 ^b
5	PhC(O)CH ₃	PhCH ₃ C=CCl ₂	86
6	○= 0	C=CCl ₂	66
7	CH ₃ (CH ₂) ₆ CHO	CH ₃ (CH ₂) ₆ CH=CCl ₂	75

Table. Synthesis of 1,1-dichloroolefins.

^aIsolated yields based on carbonyl compounds. ^bCrystallized 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 SiO₂ column chromatograpy (Et₂O/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 quenching identified aqueous to give by diethyldichloromethylphosphonate in quantitative yield⁶. 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 phosphonates⁷ 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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