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Facile synthesis of 2Z-2-Chloromethyl aryl-2-enoates :[#]

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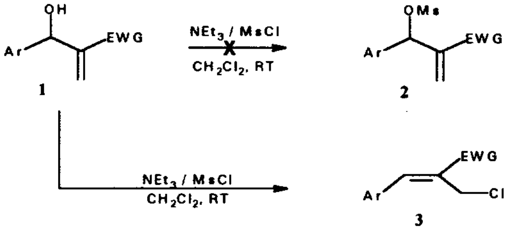
***Abstract:*:** Triethylamine - Methanesulfonyl chloride has been employed as reagent for stereoselective synthesis of 2Z-2-(Chloromethyl)aryl-2-enoates from Baylis Hillman products in good yields at room temperature. © 1997 Published by Elsevier Science Ltd.

2Z-2-(Halomethyl)alk-2-enoates[1] are an important class of compounds for the stereoselective synthesis of natural products such as α-methylene-γ-butyrolactones[2] , necic acids[3a] and α-alkylidene-β-lactams[4]. These compounds have been synthesized from 3-hydroxy-2-methylene alkanoates using 1) (HCA-PPh_3) complex[3b] 2) HBr - H_2SO_4[4] 3) NCS / NBS - Me_2S[5] 4) PBr_3[6] 5) Oxalyl chloride/ DMF/$CHCl_3$[7] 6)$CuBr_2$/ silica gel[8] and more recently by the reaction of 7) $MgBr_2$ / THF[9a] and 8) $AlCl_3$ / CH_2Cl_2[9b] with the acetate derived from the corresponding alcohol.

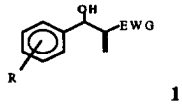
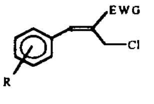


Ar = Aryl ; EWG = COOEt, COEt, SO_2Ph

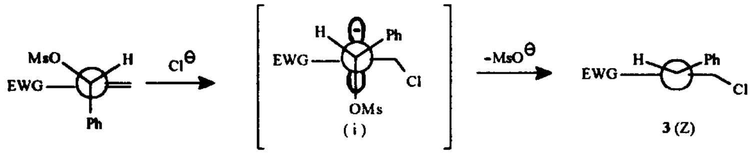
In connection with our programme on Mg / MeOH mediated transformations we needed to mesylate compound **1**. However treatment of compound **1a** with NEt_3 / MsCl furnished not **2** but the allylic rearranged chloro product **3a** in good yield. In order to see the generality of the reaction a variety of alcohols **1** were subjected to the above conditions. The results are summarised in the table.

From the table, it is evident that compound **1** gave good yields of rearranged chloro product on treatment with NEt_3 / MsCl except for entries 5 & 6 where moderate yields were obtained. However, in the case of substituted nitro compounds (entries 7 and **8**) derived from reaction of *p*-nitrobenzaldehyde with ethyl vinyl ketone and with phenyl vinyl sulfone respectively, high yields of rearranged chloro products were obtained.

Procedure : To a solution of alcohol (**1**) in dry CH_2Cl_2 (20 ml) was added triethylamine (2-5 eq) at room temperature. After 0.5 h mesyl chloride (2-5 eq) was added to the reaction mixture at 0°C. The reaction was stirred at room temperature for 1-2 days and monitored by TLC. On completion of the reaction, solvent was removed under reduced pressure and the residue purified by chromatography (SiO_2) to furnish the chloride **3**.

Entry	Subtrate		Product		NEt_3 / MsCl	% Yield
	 1		 3			
	EWG	R	EWG	R		
1.	-COOEt	a) H	-COOEt	a) H	5eq	81
		b) *p* - CN		b) *p* - CN	5eq	77
		c) *o* - Cl		c) *o* - Cl	2eq	70
		d) *p* - Cl		d) *p* - Cl	2eq	78
		e) *o* - NO_2		e) *o* - NO_2	2eq	41
		f) *p* - NO_2		f) *p* - NO_2	2 eq	50
2.	-COEt	*p* - NO_2	-COEt	*p* - NO_2	2eq	84
3.	$-SO_2Ph$	*p* - NO_2	-COEt	*p* - NO_2	2eq	90

Analogous to observation made earlier by Hoffmann[4], the exclusive formation of Z- allyl chloride can be explained by the attack of Cl^- ion in a S_N2' fashion on the mesylate **2**. The transition state (i) is the preferred one, as it involves less steric interaction between aryl and ester, giving rise to thermodynamically stable Z olefin.



In conclusion, a mild and efficient, one step synthesis of 2Z-2-(chloromethyl)aryl-2-enoates is described by treating Baylis-Hillman products 1 with NEt_3 / MsCl in good yields at room temperature.

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REFERENCES AND NOTES:

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