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A NEW METHOD FOR THE SYNTHESIS OF 2-PHENYLSULFONYLAZIRIDINES VIA THE REACTION OF α-HALOSULFONYL CARBANION TO IMINES

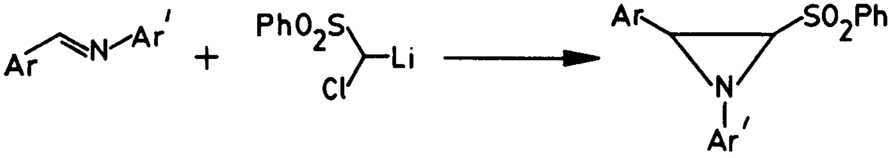
Vichai Reutrakul, Vichukorn Prapansiri and Chitchanun Panyachotipun

Department of Chemistry, Faculty of Science, Mahidol University,
Rama VI Road, Bangkok 10400, Thailand

ABSTRACT: The reaction of lithio α-chloromethyl phenyl sulfone with imines gave aziridines in good yields. The resulting aziridines were alkylated and underwent the 1,3-dipolar cycloaddition with dimethylacetylene dicarboxylate to give pyrroles in excellent yields.

Much attention has been focused on the chemistry of the α-sulfonyl carbanion due to its immense applications in organic synthesis[1]. In addition to its ability to stabilize the adjacent anionic centre, the sulfonyl group can also be removed under very mild condition[2]. Recent work on the α-halosulfonyl carbanion[3] also indicated that this species can undergo alkylation and addition reactions to give synthetically useful intermediates. Our interest in this area led us to investigate the addition of α-halosulfonyl carbanion to imines. Preliminary results are described in this letter.

The reaction of lithio α-chloromethyl phenyl sulfone with diaryl imines gave 2-phenylsulfonylaziridines[4] in excellent yields, equation (1). The method provides a new, convenient and attractive route to this interesting class of compounds. Both starting materials, imines and α-chloromethyl phenyl sulfone[5] are readily available on large scale. The results are summarized in Table I



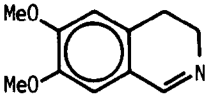
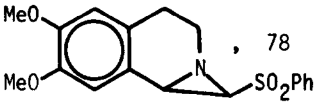
(1)

1 2 3

Table I

Entry	Imines		Products[a,b] 3, %
	Ar	Ar'	
1	Ph-	Ph-	94
2	p-ClC_6H_4-	Ph-	97
3	m-ClC_6H_4-	Ph-	83

Table I (cont.)

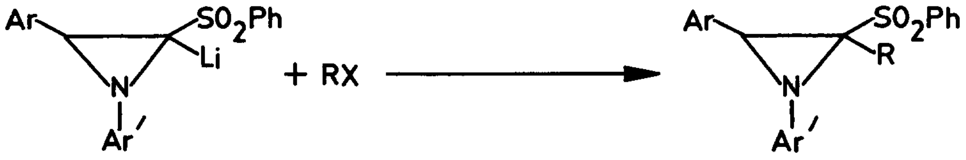
Entry	Imines $\underline{1}$ Ar	Imines $\underline{1}$ Ar'	Products[a,b] $\underline{3}$, %
4	p-NO_2-C_6H_4-	Ph-	73
5	m-$MeOC_6H_4$-	Ph-	72
6	Ph-	p-MeC_6H_4-	100
7	Ph-	p-BrC_6H_4-	97
8			 , 78

[a] All compounds were fully characterized by spectral data and elemental analysis.

[b] Products were purified by recrystallization from ethanol.

The reaction was carried out by adding imines (1 equivalent, in tetrahydrofuran, THF) to a solution of carbanion $\underline{2}$ (generated by the reaction of α-chloromethyl phenyl sulfone with lithium diisopropylamide, LDA, at -78°C in THF) at -78°C. After the addition was completed, the reaction mixture was slowly warmed to room temperature and left stirring overnight. The reaction was quenched with saturated ammonium chloride solution and the product was isolated with chloroform. Recrystallization from ethanol gave analytically pure product.

The carbanion of 2-phenylsulfonylaziridine $\underline{4}$ could also be generated and reacted with alkylating agents[4]. Our preliminary studies indicated that this is a synthetically useful process, equation (2). The results are shown in Table II.



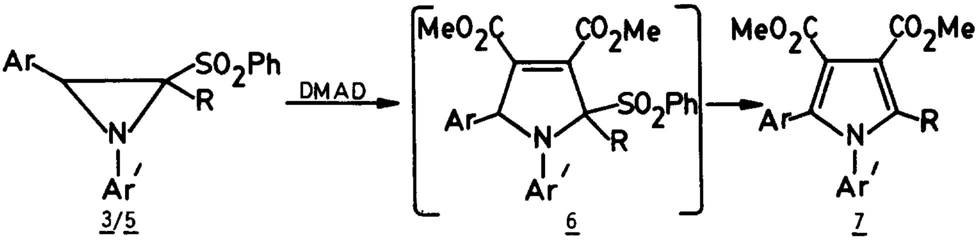
$\underline{4}$ $\underline{5}$ (2)

Table II

Aziridines			
Ar	Ar'		Alkylated Products, 5 %
m-ClC_6H_4-	Ph-	R = Me-	100
		R =  CH_2-	78
		R = $PhCH_2$-	71
		R = PhCH_2-	100
m-$MeOC_6H_4$-	Ph-	R = Me-	98
		R =  CH_2-	80
		R = $PhCH_2$-	73
		R = PhCH_2-	78

The carbanion 4 was generated by the reaction of compound 3 (1 equivalent) with LDA (1 equivalent) in THF at -78°C (to give) a dark green solution. The alkylating agent was added and the reaction mixture was stirred at the same temperature for 10 minutes before being quenched with saturated ammonium chloride. The product was isolated with chloroform and further purified by recrystallization from ethanol.

The reaction of aziridines 3 and 5 with dimethylacetylene dicarboxylate (DMAD) was also investigated. The mixture of aziridines 3/5 and excess DMAD was heated in a sealed tube at 100°C for 6 hours. The crude product was purified by preparative layer chromatography (Silica gel, E. Merck, PF_{254}, chloroform) to give pyrroles 7 in good yields, equation (3).



(3)

Ar, Ar' = Ph-, R = H; 98 % yield

Ar = p-ClC_6H_4- ; Ar' = Ph- , R = H; 100 % yield

Ar = m-ClC_6H_4- ; Ar' = Ph- , R = allyl-; 97 % yield

Ar = m-ClC_6H_4- ; Ar' = Ph- , R = Cinnamyl-; 78 % yield

We are assuming that the reaction proceeds through the addition of azomethine ylides[6] derived from the aziridines to DMAD to give the pyrrolines 6. Elimination of phenylsulfinic acid led to the formation of pyrroles. The reaction provides a convenient route to the synthesis of substituted pyrroles[7].

Further exploratory work is in progress.

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