DABCO catalyzed addition of selenosulfonates to α,β-unsaturated ketones†

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In the presence of DABCO (30 mol%), the addition of various selenosulfonates to α , β -unsaturated ketones proceeded smoothly to give the corresponding adducts in good yields under mild conditions.

Recently, we have been investigating on the Baylis–Hillman reaction of aldehydes and *N*-tosylated imines (ArCH=NTs) with activated olefins in the presence of a variety of nitrogen and phosphine Lewis bases.¹⁻³ In this paper, we wish to report a novel DABCO (1,4-diazabicyclic[2,2,2]octane) catalyzed addition of selenosulfonates to α , β -unsaturated ketones to give the corresponding adducts in good yields under mild conditions.

The addition of selenosulfonates to olefins and other carboncarbon unsaturated bonds has been known to proceed in the presence of Lewis acid BF₃·OEt₂ or through a radical reaction pattern with either photochemical initiation, or upon heating with a radical initiator such as AIBN.^{4,5} However, for α,β unsaturated ketones such as methyl vinyl ketone (MVK), no reactions occurred under these reaction conditions. During our ongoing investigation on the Baylis-Hillman reaction, we found that many nitrogen Lewis bases could catalyze the addition of selenosulfonates to MVK to give the corresponding adduct 1a in good yields at room temperature. The results are summarized in Table 1. In the presence of DABCO (30 mol%), 1a was obtained in 81% yield after 1 h in THF in the reaction of selenosulfonate (PhSeSO₂Ph) with 2.0 eq. MVK (Table 1, entry 1). Using 4-dimethylamino-pyridine (DMAP) and 1,8diazabicyclo[5.4.0]undec-7-ene (DBU) as Lewis base catalysts, this reaction proceeded quickly, but 1a was formed in 39 and 25% yields, respectively (Table 1, entries 2 and 3). Triethylamine (Et₃N) also can promote this reaction to give the adduct 1a in 42% yield after 24 h under the similar conditions (Table 1, entry 4). Phosphine Lewis bases such as triphenylphosphine, diphenylmethylphosphine, dimethylphosphine, tributylphosphine and trimethylphosphine showed no catalytic abilities for this reaction (Table 1, entries 5-9). The solvent effects have been examined by use of DABCO in toluene, ethanol, dichloromethane and ether (Et₂O). We found that THF is the solvent of choice (Table 1, entries 10–13).

Under the optimized reaction conditions, we next examined the addition of a variety of selenosulfonates to α , β -unsaturated ketones. The results are summarized in Table 2. We found that all these reactions proceeded smoothly under mild conditions to give the corresponding adducts **1b**–**1** in good to high yields after 1 h (Table 1, entries 1–11). It should be noted that for a branched α , β -unsaturated ketone (**R** = '**Pr**), the corresponding adducts **1d**, **1h** and **11** were obtained in high yields as well (Table 1, entries 3, 7, and 11).

Their structures are determined by ¹H and ¹³C NMR spectroscopic data, HRMS, and microanalyses (refer to the supple-



 Table 1
 Lewis base-catalyzed addition of selenosulfonate (1.0 eq.) to MVK (2.0 eq.)

				Yield/%a	
Entry	Lewis base	Solvent	Time/h ^b	1a	
1	DABCO	THF	1	81	
2	DMAP	THF	1/2	39	
3	DBU	THF	1/6	25	
4	Et ₃ N	THF	24	42	
5	PPh ₃	THF	24	No reaction	
6	PPh ₂ Me	THF	24	No reaction	
7	$PPhMe_2$	THF	24	No reaction	
8	PBu ₃	THF	24	Trace	
9	PMe ₃	THF	24	Trace	
10	DABCO	Toluene	2/3	39	
11	DABCO	EtOH	1/2	c	
12	DABCO	CH_2Cl_2	1/2	59	
13	DABCO	Et ₂ O	1/2	44	

^{*a*} Isolated yields. ^{*b*} The reaction time to consume all of the starting materials. ^{*c*} Complex reaction from which no products could be identified.

Table 2 DABCO-catalyzed addition of selenosulfonates (1.0 eq.) to $\alpha \beta$ -unsaturated ketones (2.0 eq.)

		THF, r.t., '	1h 📗	
			1 0	
			Yield /% ^a	
Entry	Ar	R	1	
1	C ₆ H ₅	Et	1b , 81	
2	C_6H_5	Ph	1c, 75	
3	C_6H_5	<i>i</i> -Pr	1d, 83	
4	p-MeC ₆ H ₄	Me	1e, 87	
5	$p-MeC_6H_4$	Et	1f, 85	
6	p-MeC ₆ H ₄	Ph	1g, 85	
7	$p-MeC_6H_4$	<i>i</i> -Pr	1h, 80	
8	p-MeOC ₆ H ₄	Me	1i , 90	
9	p-MeOC ₆ H ₄	Et	1j , 93	
10	p-MeOC ₆ H ₄	Ph	1k, 70	
11	<i>p</i> -MeOC ₆ H ₄	<i>i</i> -Pr	11.94	

mentary information). The obtained adducts **1** can undergo a selenoxide elimination upon oxidation with hydrogen peroxide in THF to afford the corresponding (E)- β -phenylsulfonylenones **2** within 1 h in high yields (Scheme 1).⁶

1620

[†] Electronic supplementary information (ESI) available: spectroscopic data, HRMS, analytical data, experimental procedures. See http://www.rsc.org/suppdata/ob/b5/b501942g/



Scheme 1 Selenoxide elimination with hydrogen peroxide.

The mechanism for this unusual DABCO catalysed addition reaction of selenosulfonates to α,β -unsaturated ketones has not been unequivocally established, but on the basis of previous investigations⁴ and the generally accepted reaction mechanism for Baylis–Hillman reaction,¹⁻³ one plausible explanation is proposed in Scheme 2. The nucleophilic addition of the *in situ* formed zwitterionic enolate **A**, derived from DABCO and the corresponding α,β -unsaturated ketone, to the selenosulfonate produces the intermediate **B**. The generated PhSO₂⁻ species attacks at the terminal carbon of α,β -unsaturated ketones of the intermediate **B** to give the final product and regenerate DABCO Lewis base catalyst (Scheme 2).⁷



Scheme 2 The plausibel reaction mechanism.

The control experiment has confirmed that this addition reaction under the optimized conditions was unaffected by the addition of the radical inhibitors such as TEMPO and 3 eq. 2,6-di-*tert*-butyl-4-methylphenol (BHT), rendering unlikely the intervention of a radical pathway.

In conclusion, we have found a novel DABCO catalyzed addition of selenosulfonates to a variety of α,β -unsaturated ketones to give the adducts **1** in good to high yields within short reaction time under mild conditions. This synthetic approach also provides a facile route to the synthesis of (E)- β -phenylsulfonylenones **2**. Efforts are in progress to elucidate the mechanistic details of this reaction and to disclose its scope and limitations.

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