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Transition metal-free activation of allylic acetates toward regioselective S-allylation of thiols

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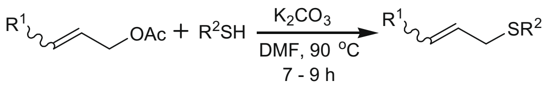
A B S T R A C T

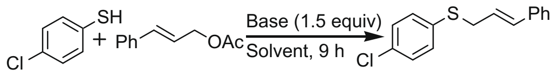
Allylic acetates have been used as allylating agents under transition metal-free condition toward an economical and sustainable regioselective S-allylation of aromatic and aliphatic thiols in the presence of potassium carbonate in DMF.

The nucleophilic substitution of allylic compounds is a useful process in organic synthesis and is frequently used as an important tool in the synthesis of complex organic molecules.[1] Usually these reactions are performed using allyl alcohol derivatives[2a–j] or allyl halides[2k–o] catalyzed by a variety of transition metal (Pd, Ni, and Ru) complexes.[2] Allyl acetates are preferred as allylating agents because of their easy availability and configurational stability and on the other hand, the limitation of more highly activated allyl halides and tosylates.[2j] However, use of less reactive allyl acetates requires the involvement of a transition metal catalyst to activate the allylic system toward nucleophilic addition. Although metal-catalyzed allylation reaction with carbon, oxygen, and nitrogen nucleophiles is well studied,[3] allylation of sulfur nucleophiles is more challenging probably because of deactivation of metal catalyst by sulfur compounds due to their strong co-ordinating properties.[4a,b,d] Moreover, metal-catalyzed allylations often led to a mixture of regioisomers.[4] Although a few transition metal-free Lewis/protic acid-catalyzed procedures have been developed using allyl alcohols, these reactions also ended up with the formation of regioisomers.[5] Thus, a transition metal-free regioselective allylation of thiols is appreciated. We report here a simple and efficient protocol for highly regioselective allylation of thiols with allyl acetates in the presence of a mild base K_2CO_3 in DMF (Scheme 1). In our attempts for allylic alkylation of thiols by allyl acetates we discovered that the reaction does not require any transition metal



Scheme 1. Allylation of thiols with allylic acetates.

Table 1
Standardization of the reaction condition for S-allylation



Entry	Base	Solvent	Temp. (°C)	Yield (%)
1	Na_2CO_3	DMF	90	70
2	K_3PO_4	DMF	90	53
3	NaOH	DMF	90	15
4	$\mathbf{K_2CO_3}$	**DMF**	**90**	**88** (***E***:***Z*** **= 100:0**)
5	K_2CO_3	DMF	70	69
6	K_2CO_3	DMF	rt	0
7	K_2CO_3	DMF	90	76[a]
8	K_2CO_3	DMF	90	82[b]
9	No base	DMF	90	0
10	K_2CO_3	THF	Reflux	Trace
11	K_2CO_3	H_2O	90	74
12	K_2CO_3	CH_3CN	Reflux	66
13	K_2CO_3	Toluene	90	0

[a] 1 equiv of base was used.
[b] Reaction was carried out for 5 h.

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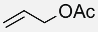
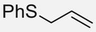
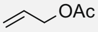
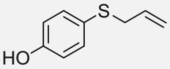
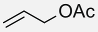
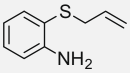
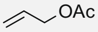
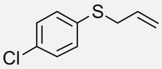
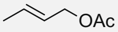
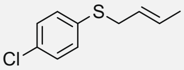
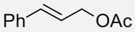
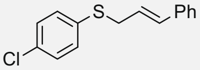
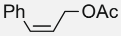
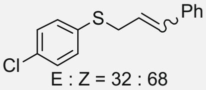
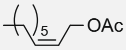
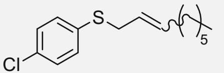
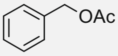
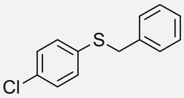
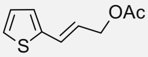
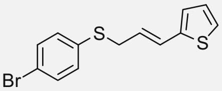
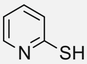
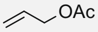
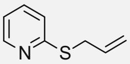
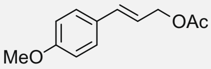
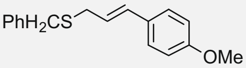
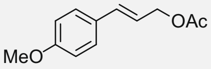
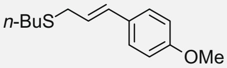
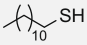
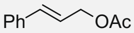
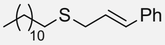
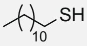
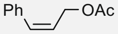
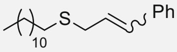
catalyst. We rationalized that thiols being stronger nucleophiles compared to amines and alcohols[6] are capable of adding directly to the allylic system without any pre-activation by metal.

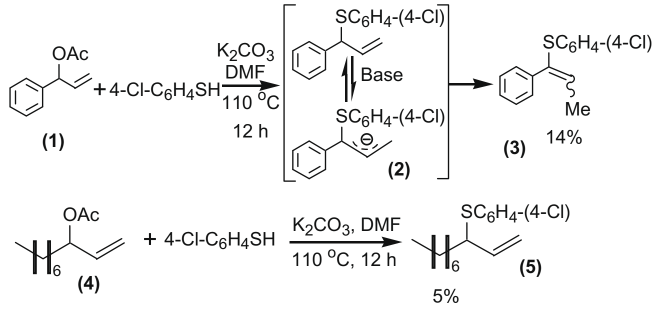
To standardize the reaction conditions a representative reaction of 4-chloro thiophenol and cinnamyl acetate was carried out with a variety of bases in different solvents at varied temperature and time. The best result was obtained using 1.5 equiv of K_2CO_3 in DMF at 90 °C for 9 h (Table 1). As illustrated in Table 1, the reaction did not proceed at all in the absence of base. Probably, the base K_2CO_3 accelerates the thiol toward nucleophilic attack generating the more nucleophilic thiolate anion and also participates in the neutralization of acetic acid formed during the reaction.

The experimental procedure is very simple.[7] A mixture of allyl acetate and thiol was heated in DMF at 90 °C in the presence of K_2CO_3 for a period of time as required for the completion of the reaction (TLC). A wide range of diversely substituted thiols underwent allylations by a variety of allyl acetates to provide the corresponding allyl sulfides. The results are summarized in Table 2. The aromatic, heteroaromatic, and aliphatic thiols participated in this reaction uniformly. In addition to allyl acetate, substituted alkyl, aryl, and heteroaryl allylic acetates such as crotyl, cinnamyl, and thienyl also underwent reactions without any difficulty. The reactions proceed with high regioselectivity giving only linear allylic sulfides without any exception. Several substituents such as Cl, Br, OH, NH_2, and OMe on the aromatic rings of thiols and allyl acetates are compatible with this procedure. The *trans*-allyl acetates (Table 2, entries 5, 6, 10, 12–14) retain their stereochemistry to produce the (*E*)-products; however, the *cis* allyl acetates (Table 2, entries 7, 8, and 15) lead to the mixture of (*Z*)- and (*E*)-isomers with (*Z*)-allyl sulfides predominating. It was observed that when this mixture of (*E*)- and (*Z*)-isomers was subjected to heating at 100 °C in DMF for 36 h in the presence of K_2CO_3, the (*Z*)-isomer was totally converted to (*E*)-isomer (Eq. (1)). Thus, it is likely that *cis* allyl acetate initially produces (*Z*)-isomer which is partially transformed into thermodynamically more stable (*E*)-isomer under the reaction conditions.

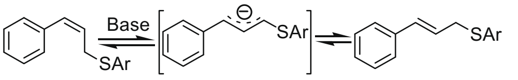
Table 2
Allylation of thiols with various allylic acetates

Entry	Thiol	Allylic acetate	Product	Time (h)	Yield[a] (%)	Ref.
1	PhSH			8	86	4d
2	4-OH–C_6H_4SH			8	78	4a
3	2-NH_2–C_6H_4SH			8	75	8
4	4-Cl–C_6H_4SH			8	90	9
5	4-Cl–C_6H_4SH			7	77	10
6	4-Cl–C_6H_4SH			9	88	
7	4-Cl–C_6H_4SH		 E : Z = 32 : 68	9	85	
8	4-Cl–C_6H_4SH		 E : Z = 17 : 83	9	82	
9	4-Cl–C_6H_4SH			9	85	11
10	4-Br–C_6H_4SH			8	78	
11				8	89	4a
12	$PhCH_2SH$			9	73	
13	*n*-BuSH			7	75	
14				9	83	
15			 E : Z = 27 : 73	9	84	

[a] Isolated yields of pure products.



Scheme 2. Reaction of 4-chlorothiophenol with secondary/branched allylic acetates.



(1)

The reaction is believed to proceed through S_N2 path with an α-addition of the thiolate anion leading to linear allylic sulfide as a sole product. It has been observed that this procedure is not very effective for secondary/branched allylic acetates probably due to steric factors. When an aromatic-branched allyl acetate **1** was heated with 4-chloro thiophenol at 110 °C for 12 h under usual reaction conditions a vinylic sulfide **3** was isolated in low yield (14%). Possibly, the compound **3** resulted from the α-attack of thiol followed by isomerization to the conjugated system. For generalization, when an aliphatic-branched allyl acetate **4** was subjected to similar treatment, the corresponding allylic sulfide was obtained (5%) by the α-addition (Scheme 2). The absence of a phenyl ring adjacent to the double bond does not facilitate isomerization in this case. Thus, exclusive α-addition to all allyl acetates supports the S_N2 path.

A Hammett correlation plot of log I (where I represents the ratio of the peak intensity of the product with that of the starting material in the ^{1}H NMR spectrum of crude reaction mixture after an intermediate time period of 1.25 h) versus σ (substituent constant) for the reaction of 4-chlorothiophenol with different substituted cinnamyl acetates under identical reaction conditions (Figure 1) shows a linear correlation with a small positive slope (ρ = 0.225) which suggests the S_N2 reaction path.

In general, the reactions are very clean and high yielding. In addition to regioselectivity this procedure also shows chemoselectivity. In S-allylations of 2-aminothiophenol (Table 2, entry 3) and 4-hydroxythiophenol (Table 2, entry 2) no N- or O-allylation was observed even in the presence of excess allyl acetate.

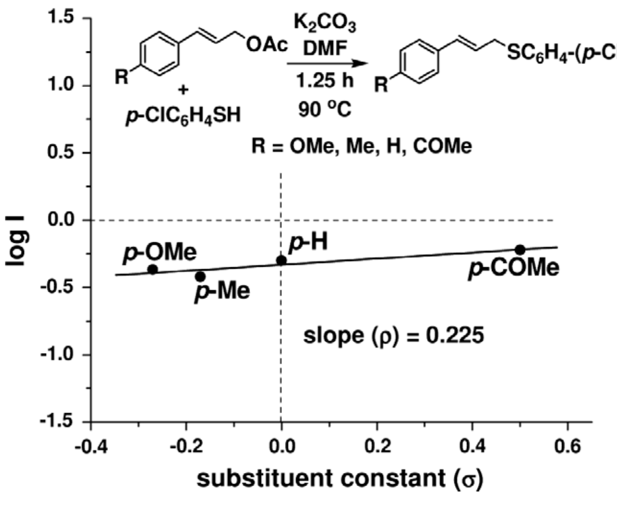


Figure 1. Hammett Plot.

In summary, we have developed a transition metal-free simple protocol for S-allylation of thiols with allyl acetates. The reactions are highly regio- and chemoselective. The complete retention of stereochemistry was maintained in the reactions of *trans*-allyl acetates. This procedure has general applicability to the reactions of a wide variety of aromatic, aliphatic, and heteroaromatic thiols with aliphatic, aromatic, and heteroaromatic allylic acetates. To the best of our knowledge, we are not aware of any transition metal-free S-allylation of thiols by allylic acetates with such a wide scope. On extensive literature search on S-allylations by allylic acetates we have found only two reports of transition metal-free allylation of thiols using diallyl carbonate[12a] and Baylis–Hillman acetates.[12b] However, no generalizations have been made.[12] Nevertheless, because of its simplicity and low cost in operation and use of environmentally benign reagents, this procedure will provide an easy access to synthetically useful allylic sulfides[1c,13] by S-allylation of thiols.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.02.015.

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7. *General experimental procedure for S-allylation of thiols with allyl acetates. Representative procedure for the reaction of cinnamyl acetate and 4-chlorothiophenol* (Table 2, *entry 6*): A mixture of cinnamyl acetate (1 mmol, 176 mg), 4-chlorothiophenol (1 mmol, 145 mg) and K_2CO_3 (1.5 mmol, 207 mg) was heated in DMF (2 mL) at 90 °C for 9 h under argon. After completion of the

reaction (TLC), the reaction mixture was diluted with ether. The organic layer was dried over anhydrous Na_2SO_4 and was concentrated under reduced pressure. The product was obtained as a pure white solid (mp 84–87 °C) after column chromatography using hexane (229 mg, 88%). The compound was characterized by its spectroscopic data and elemental analysis, IR (KBr): 2926, 2854, 1475, 1446, 1388, 966, 808 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.60 (2H, d, J = 7.0 Hz), 6.09–6.19 (1H, m), 6.34 (1H, d, J = 15.7 Hz), 7.15–7.24 (9H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.4, 124.7, 126.4 (2C), 127.8, 128.6 (2C), 129.0 (2C), 131.8 (2C), 132.6, 133.1, 134.3, 136.6; Anal. Calcd for $C_{15}H_{13}ClS$: C, 69.08; H, 5.02. Found: C, 69.11; H, 5.06. This procedure was followed for all the reactions listed in Table 2. Many of these products are known compounds and were easily identified by comparison of their spectroscopic data with those reported (see Refs. in Table 2). The unknown compounds (Table 2, entries 7, 8, 10, 12–15) were properly characterized by their spectroscopic data (IR, ^1H NMR, ^{13}C NMR, and HRMS) which are presented below in order of their entries. The purity of all compounds was also checked by ^1H NMR and ^{13}C NMR.

1-Chloro-4-(3-phenyl-allylsulfanyl)-benzene (as a mixture of E and Z isomers) (Table 2, *entry 7*): colorless viscous liquid; IR (neat): 3024, 2904, 1475, 1448, 1388, 1095, 968, 810 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.70 (2H, d, J = 7.0 Hz), 3.80 (2H, d, J = 7.7 Hz), 5.76–5.82 (1H, m), 6.16–6.29 (1H, m), 6.44 (1H, d, J = 15.7 Hz), 6.60 (1H, d, J = 11.3 Hz), 7.16–7.40 (18H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 32.24, 37.41, 124.72, 126.41 (2C), 126.78, 127.35, 127.76, 128.42 (2C), 128.63 (2C), 128.77 (2C), 128.95 (2C), 129.03 (2C), 130.89 (2C), 131.76 (2C), 132.16, 132.35, 132.55, 133.12, 134.38, 134.49, 136.34, 136.61; Anal. Calcd. for $C_{15}H_{13}ClS$: C, 69.08; H, 5.02. Found: C, 69.12; H, 5.05.

1-Chloro-4-non-2-enylsulfanyl-benzene (as a mixture of E and Z isomers) (Table 2, *entry 8*): colorless liquid; IR (neat): 2955, 2926, 2854, 1475, 1388, 1222, 1095, 1012, 964, 815 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.90 (6H, t, J = 6.9 Hz), 1.26–1.32 (16H, m), 1.96–1.98 (4H, m), 3.48 (2H, d, J = 6.0 Hz), 3.54 (2H, d, J = 6.4 Hz), 5.46–5.55 (4H, m), 7.22–7.30 (8H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.21 (2C), 22.73 (2C), 27.34, 28.82, 29.08 (2C), 29.24, 29.52, 31.71, 31.81, 32.35, 36.89, 124.19, 124.64, 126.03 (2C), 128.90 (2C), 129.00 (2C), 131.47 (2C), 131.65 (2C), 132.42, 134.14, 134.97, 135.07; HRMS Calcd for $C_{15}H_{21}ClSK$ ($[M+K]^+$) 307.0690; Found: 307.0964.

2-[3-(4-Bromo-phenylsulfanyl)-propenyl]-thiophene (Table 2, *entry 10*): pale yellow solid, mp 89–91 °C; IR (KBr): 3024, 2955, 1471, 1384, 1089, 1003, 945, 806 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.65 (2H, d, J = 7.2 Hz), 6.05–6.12 (1H, m), 6.55 (1H, d, J = 15.5 Hz), 6.90–6.96 (2H, m), 7.14–7.16 (1H, m), 7.24 (2H, d, J = 8.4 Hz), 7.41 (2H, d, J = 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.0, 120.4, 124.1, 124.3, 125.6, 126.1, 127.3, 131.9 (4C), 134.9, 141.4; HRMS Calcd for $C_{13}H_{11}BrS_2K$ ($[M+K]^+$) 348.9123; Found: 348.8244.

1-(3-Benzylsulfanyl-propenyl)-4-methoxy-benzene (Table 2, *entry 12*): pale yellow liquid; IR (neat): 3028, 2908, 2833, 1606, 1510, 1286, 1247, 1174, 1031, 964, 823 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 3.23 (2H, d, J = 7.3 Hz), 3.73 (2H, s), 3.83 (3H, s), 6.01–6.11 (1H, m), 6.38 (1H, d, J = 15.6 Hz), 6.89 (2H, d, J = 8.6 Hz), 7.26–7.39 (7H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 33.9, 35.2, 55.3, 114.1 (2C), 123.6, 127.0, 127.6 (2C), 128.6 (2C), 129.1 (2C), 129.6, 132.0, 138.5, 159.3; HRMS Calcd for $C_{17}H_{18}OSK$ ($[M+K]^+$) 309.0715; Found: 308.9709.

1-(3-Butylsulfanyl-propenyl)-4-methoxy-benzene (Table 2, *entry 13*): colorless liquid; IR (neat): 2956, 2929, 1606, 1510, 1462, 1286, 1249, 1176, 1033, 964, 831 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.90 (3H, t, J = 7.2 Hz), 1.36–1.44 (2H, m), 1.52–1.60 (2H, m), 2.49 (2H, t, J = 7.5 Hz), 3.28 (2H, dd, J_1 = 7.3 Hz, J_2 = 1.1 Hz), 3.79 (3H, s), 5.99–6.09 (1H, m), 6.37 (1H, d, J = 15.6 Hz), 6.85 (2H, d, J = 8.7 Hz), 7.30 (2H, d, J = 8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.7, 22.0, 30.5, 31.5, 34.4, 55.3, 114.0 (2C), 124.0, 127.4 (2C), 129.6, 131.4, 159.1; HRMS Calcd for $C_{14}H_{20}OSK$ ($[M+K]^+$) 275.0872; Found: 275.0317.

E-(3-Dodecylsulfanyl-propenyl)-benzene (Table 2, *entry 14*): colorless liquid; IR (neat): 2926, 2852, 1460, 1217, 962, 758 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.89 (3H, t, J = 6.9 Hz), 1.26–1.39 (18H, m), 1.56–1.61 (2H, m), 2.49 (2H, t, J = 7.5 Hz), 3.30 (2H, dd, J_1 = 7.3 Hz, J_2 = 1.1 Hz), 6.16–6.24 (1H, m), 6.43 (1H, d, J = 15.7 Hz), 7.23–7.39 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.25, 22.82, 29.03, 29.30, 29.40, 29.55 (2C), 29.66, 29.76, 29.80, 30.93, 32.05, 34.45, 126.40 (3C), 127.60, 128.68 (2C), 132.01, 136.95; HRMS Calcd for $C_{21}H_{34}SK$ ($[M+K]^+$) 357.2018; Found: 357.2549.

(3-Dodecylsulfanyl-propenyl)-benzene (as a mixture of E and Z isomers) (Table 2, *entry 15*): colorless liquid; IR (neat): 2924, 2852, 1492, 1464, 1446, 1220, 1074, 962, 808 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (6H, t, J = 6.7 Hz), 1.29–1.63 (40H, m), 2.45–2.53 (4H, m), 3.32 (2H, d, J = 7.3 Hz), 3.42 (2H, dd, J_1 = 7.8 Hz, J_2 = 1.1 Hz), 5.72–5.82 (1H, m), 6.16–6.26 (1H, m), 6.45 (1H, d, J = 15.7 Hz), 6.59 (1H, d, J = 11.4 Hz), 7.21–7.38 (10H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.92, 29.02 (2C), 29.33 (2C), 29.40, 29.50 (4C), 29.63 (2C), 29.70 (4C), 29.80 (4C), 30.91, 31.55, 32.04, 32.66, 34.43, 39.55, 126.40 (3C), 127.09, 127.56, 128.49 (2C), 128.52, 128.65 (2C), 128.89 (2C), 131.30, 132.00, 136.76 (2C); HRMS Calcd for $C_{21}H_{34}SK$ ($[M+K]^+$) 357.2018; Found: 357.0979.

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