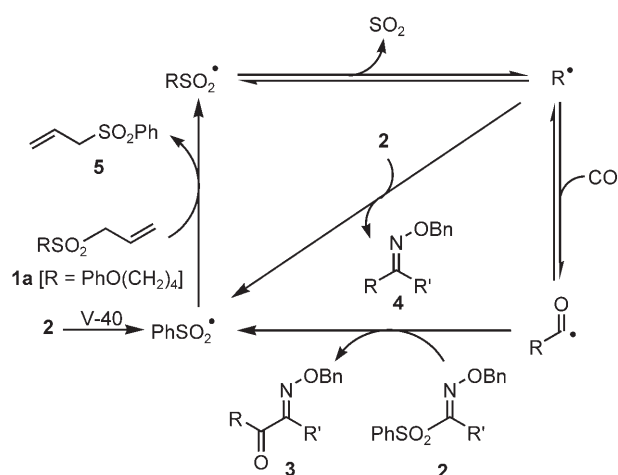
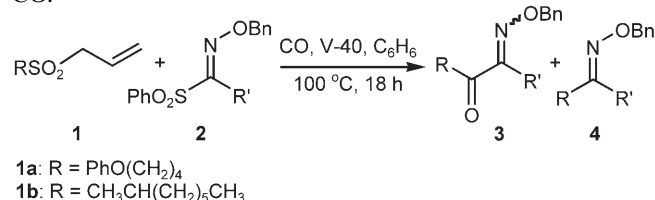


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Scheme 1. Tin-free radical carbonylation of an alkyl allyl sulfone with phenylsulfonyl oxime ether **2**.

Table 1. The effects of concentration of **1** and pressure of CO.



Alkyl allyl sulfone 1	Phenylsulfonyl oxime ether 2	Conc. [M]	CO [atm]	Yield [%]		
				3	4	1
1a	2a	0.05	95	94	0	0
		0.03	95	93	0	0
		0.01	95	74	0	21
		0.05	50	58	19	17
	2b	0.03	50	64	12	19
		0.03	50	93	0	0
1b	2a	0.03	30	94	0	0
		0.03	130	72	24	0
		0.01	130	74	19	0
		0.05	95	41	49	0
	2b	0.03	95	60	35	0
		0.01	95	64	30	0
		0.03	130	91	0	0
		0.03	95	75	0	21
		0.01	95	54	0	38

oxime ether by-product **4**, resulting from the direct addition of an alkyl radical onto **2a** prior to radical carbonylation, was formed at the lower pressure of CO (95 atm *versus* 50 atm). Second, when the reaction was repeated with acceptor **2b** under 50 atm of CO, the desired product was isolated in high yield without the formation of a by-product, indicating that

2b is more reactive than **2a** towards an acyl radical. Finally, although a diluted condition reduced the formation of by-product **4**, the chain propagation became less efficient, resulting in the recovery of some starting material. Thus, for the primary alkyl allyl sulfone precursor, the remaining reactions were carried out with **2** (95 atm CO for **2a** and 30 atm CO for **2b**, 1.5 equivs.) and V-40 (0.2 equivs.) as initiator in a pressurized autoclave in benzene (0.03 M) at 100 °C for 18 h.

When the reaction was repeated with the secondary alkyl allyl sulfone precursor **1b** using the less reactive **2a**, a significant amount of by-product **4** was isolated. Since secondary alkyl radicals are more stable than primary alkyl radicals, the radical carbonylation of secondary alkyl radicals is slower and less efficient than that of primary alkyl radicals,^[11] thereby giving the secondary alkyl radicals more chance to react with **2a** prior to radical carbonylation to yield **3**. At 95 atm of CO in benzene (0.01 M), a 64:30 mixture of the acylated oxime ether and the oxime ether was isolated. When the same reaction was repeated at a higher pressure of CO (130 atm) for 18 h, the formation of the oxime ether was reduced to some extent, yielding a 74:19 mixture of **3** and **4**. However, the use of more reactive **2b** obviates the problem of the formation of **4**. When the same reaction was repeated using **2b** at 95 atm of CO in benzene (0.03 M) at 100 °C, acylated oxime ether **3** was isolated in 75 % yield along with recovery of the starting material (21 %). By increasing CO pressure to 130 atm, the starting material was consumed completely.

Table 2 summarizes the experimental results and illustrates the efficiency and scope of the present method. Primary alkyl allyl sulfone precursors worked well using phenylsulfonyl oxime ether **2a** and **2b**, yielding the corresponding acylated oxime ethers in high yields (entries 1–5). Substrate **2a** required a higher CO pressure than **2b** (95 atm for **2a** *versus* 30 atm for **2b**) in benzene (0.03 M). There was no indication of the formation of oxime ether **4**. However, as mentioned previously, secondary alkyl allyl sulfone precursors required a high CO pressure (130 atm) to obviate the problem of the formation of a by-product or recovery of some starting material (entries 6–8). Under the present conditions, when **2b** was used, acylated oxime ethers were obtained in high yields. In the case of **2a**, a small amount of the by-product or some starting material was obtained together with the desired acylated products (entries 6 and 8). As we anticipated, tertiary alkyl radicals gave even more direct addition by-product (entry 9) due to a more favored reverse reaction in the carbonylation step.^[11] In the case of a benzylic radical, the benzylic radical did not undergo carbonylation and reacted with **2a** to give oxime ether in 56 % yield along with recovery of the starting material (40 %) (entry 10).

Table 2. Tin-free radical carbonylation of alkyl allyl sulfones.

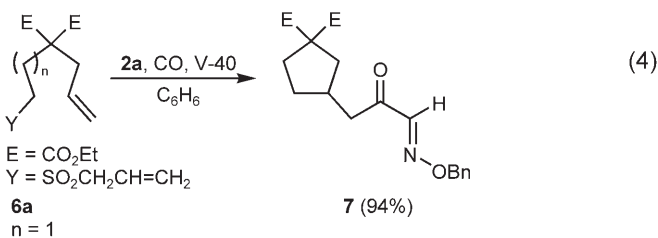
Entry	Alkyl allyl sulfone Y = SO ₂ CH ₂ CH=CH ₂	Oxime 2 /CO	Yield [%] ^[a]
1		2a /95 atm 2b /30 atm	98 88
2		2a /95 atm 2b /30 atm	96 89
3		2a /95 atm 2b /30 atm	90 87
4		2a /95 atm 2b /30 atm	97 93
5		2a /95 atm 2b /30 atm	87 81
6		2a /130 atm 2b /130 atm	81(8) 90
7		2a /130 atm 2b /130 atm	82 95
8		2a /130 atm 2b /130 atm	76 ^[b] 96
9		2b /130 atm	32(62)
10		2a /130 atm	0(56) ^[c]

^[a] The numbers in parentheses indicate the yield of oxime ether **4**.

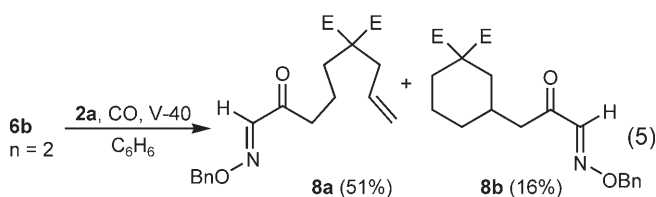
^[b] Allyl sulfone **1** (10 %) was recovered.

^[c] Allyl sulfone **1** (40 %) was also recovered.

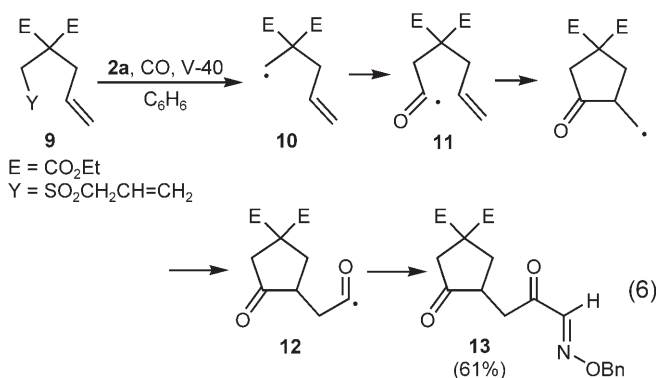
Sequential radical reactions involving cyclization followed by carbonylation and the subsequent quenching with **2a** afforded product **7** in 94 % yield [Eq. (4)]. However, in the case of **6b**, a 16:51 mixture



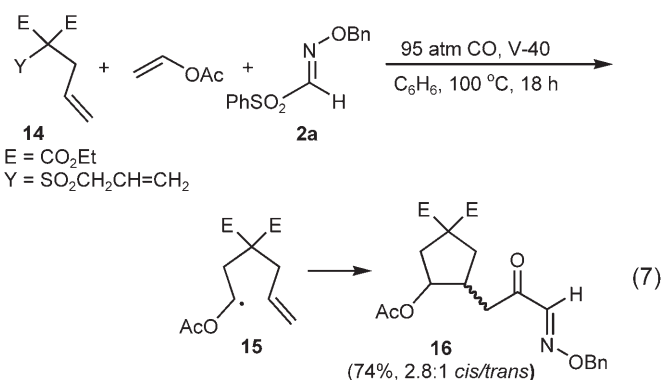
of two products was isolated in favor of the direct carbonylation product, apparently due to the competition between 6-*exo* ring closure and the direct carbonylation [Eq. (5)]. We next explored a double carbony-



lation, which involves a 5-step sequence comprising radical carbonylation of radical intermediate **10** followed by 5-*exo* ring closure of **11**, CO-trapping, and the subsequent quenching of acyl radical **12** with **2a** to afford cyclopentanone derivative **13** in 61 % yield [Eq. (6)].^[12] Finally, the four-component coupling re-



action comprising **14**, vinyl acetate, CO, and **2a** was also successful, where **16** was isolated in 74 % yield [Eq. (7)].



In summary, based on the successful tin-free radical carbonylation using alkyl allyl sulfone precursors, we have developed a very efficient method for the synthesis of acylated oxime ethers using phenylsulfonyl oxime ether **2a** or **2b** as a trapping agent.

Experimental Section

Typical Procedure

Benzene (10 mL), 4-phenoxybutyl allyl sulfone (76 mg, 0.3 mmol), **2a** (124 mg, 0.45 mmol), and V-40 (15 mg, 0.06 mmol) were placed in a 50-mL stainless steel autoclave. The autoclave was sealed, purged three times with 10 atm of CO, pressurized with 95 atm of CO, and then heated at 100°C with stirring for 18 h. After excess CO was discharged at room temperature, the solvent was removed under reduced pressure. The residue was purified by a silica gel column chromatography using ethyl acetate and *n*-hexane (1:20) as eluant to give 2-oxo-6-phenoxyhexanal O-benzyl oxime (**3a**); yield: 87 mg (93%); ¹H NMR (CDCl₃, 400 MHz): δ = 1.79–1.83 (m, 4H), 2.82–2.86 (m, 2H), 3.94–3.97 (m, 2H), 5.25 (s, 2H), 6.87–6.96 (m, 3H), 7.26–7.30 (m, 2H), 7.35–7.38 (m, 5H), 7.51 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ = 20.4, 28.7, 37.4, 67.3, 77.8, 114.5, 120.6, 128.4, 128.5, 128.6, 129.4, 136.2, 158.9, 198.1; IR (polymer): ν = 3033, 2939, 1692, 1600, 1587, 1497, 1455, 1246, 1009 cm⁻¹; HR-MS: *m/z* = 311.1525, calcd for C₁₉H₂₁NO₃ (M⁺): 311.1521.

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