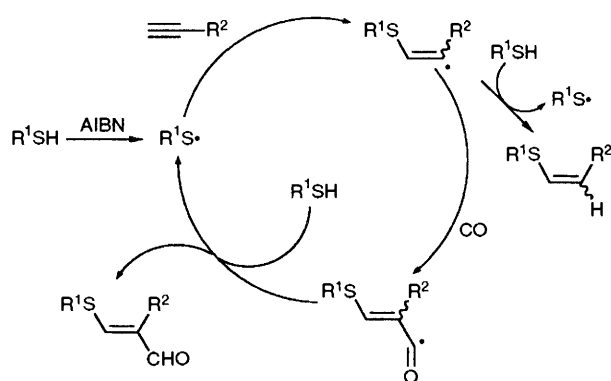




**Table 1** Radical carbonylation of alkynes in the presence of thiol

Thiol R <sup>1</sup>	Alkyne R <sup>2</sup>	Yield (%) <sup>a</sup>	
		1	2
C <sub>6</sub> H <sub>13</sub>	C <sub>8</sub> H <sub>17</sub>	70	9
c-C <sub>6</sub> H <sub>11</sub>	C <sub>8</sub> H <sub>17</sub>	68	7
Bu <sup>t</sup>	C <sub>8</sub> H <sub>17</sub>	60	0
Ph	C <sub>8</sub> H <sub>17</sub>	39	28
EtO <sub>2</sub> CCH <sub>2</sub>	C <sub>8</sub> H <sub>17</sub>	69	15
C <sub>6</sub> H <sub>13</sub>	Ph	41	0
Bu <sup>t</sup>	Ph <sup>b</sup>	60	0
C <sub>6</sub> H <sub>13</sub>	CH <sub>2</sub> CH <sub>2</sub> OAc	54	10

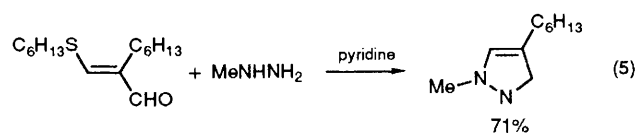
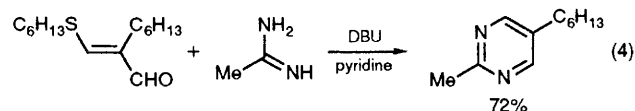
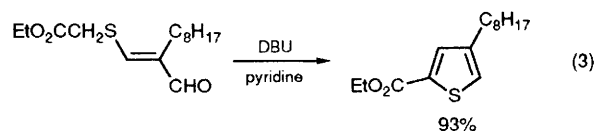
<sup>a</sup> Isolated yields. <sup>b</sup> Benzoylperoxide was used as radical initiator.

**Scheme 1**

The reactions of alkynes with thiols and carbon monoxide were carried out as follows: A solution of alkyne (0.5 mmol), thiol (1.2–1.5 equiv.), and azobis(isobutyronitrile) (AIBN) (0.4 equiv.) in benzene (50 ml) was placed in an autoclave. Carbon monoxide gas was introduced (80 atm) and the mixture was heated at 100°C for 10 h. Evaporation of the solvent followed by flash chromatography afforded the carbonylation products **1** together with alkenyl sulfides **2**<sup>6</sup> (Table 1). Various thiols including hexyl mercaptan, cyclohexyl mercaptan, *tert*-butyl mercaptan, and ethyl thioglycolate were effective, but the use of thiophenol resulted in low selectivity of the carbonylation product **1** over the alkenyl sulfides **2**.

It is noteworthy that the carbonylation products **1** were obtained as a single stereoisomer. The stereochemistry of **1** (R<sup>1</sup> = *c*-C<sub>6</sub>H<sub>11</sub>, R<sup>2</sup> = C<sub>8</sub>H<sub>17</sub>) was determined by <sup>1</sup>H NMR spectroscopy. Since the NOE (nuclear Overhauser effect) was observed between the aldehyde proton and the vinyl proton, the stereochemistry of the carbonylation product was determined as *E*.

We propose the following radical chain mechanism (Scheme 1). The alkylthio radical adds to the alkyne to give the β-alkylthio alkenyl radical. The reaction of this radical with carbon monoxide followed by hydrogen abstraction from the thiol gives the carbonylation product and regenerates the alkylthio radical. The alkenyl radical intermediate seems to be a mixture of *E* and *Z* isomers because isomerization of such radicals is known to be very fast.<sup>7</sup> Alkenyl sulfides **2** obtained as byproducts were a mixture of *E* and *Z* isomers. However, only the *E* isomer of the carbonylation product **1** was obtained in the present reaction. Probably there is an equilibration



between the *E* and the *Z* isomers of **1** in the presence of alkylthiol or alkylthio radicals, and the more stable *E*-**1** was obtained as a thermodynamic product.

2-Alkyl-3-alkylthiopropenals obtained by the present reaction are useful intermediates in the synthesis of heterocyclic compounds. For example, 2-octyl-3-(ethoxycarbonylmethylthio)propenal, which was prepared from dec-1-yne and ethyl thioglycolate, cyclized intramolecularly with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in pyridine to give 2,4-disubstituted thiophene in high yield [eqn. (3)].<sup>8</sup> 2-Alkyl-3-alkylthiopropenals can also be converted into 2,5-disubstituted pyrimidines<sup>9</sup> or 1,4-disubstituted pyrazoles<sup>9</sup> by the reaction with acetamide or methylhydrazine, respectively [eqns. (4) and (5)].

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