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SULFUR-ASSISTED O-CARBONYLATION OF ALCOHOLS WITH CARBON MONOXIDE IN THE PRESENCE OF DBU

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The first example of sulfur-assisted O-carbonylation is described. Alcohols react with carbon monoxide, elemental sulfur, and alkyl halides in the presence of DBU to give S-alkyl carbonothioates selectively in good to excellent yields.

Elemental sulfur promoted carbonylation using carbon monoxide has been hitherto limited to N-carbonylation of amines. For example, urea derivatives¹⁾ and S-alkyl carbamothicates²⁾ were shown to form under pressurized carbon monoxide at high temperature. However, because of low reactivity of a hydroxyl group, sulfur-assisted O-carbonylation of alcohols with carbon monoxide would not be expected to proceed satisfactorily under the mild conditions.

In the course of our studies on sulfur-assisted carbonylation with carbon monoxide, we recently reported C-carbonylation of 2'-hydroxyacetophenones to afford 4-hydroxycoumarins in the presence of tertiary amine.³⁾ We herein wish to report a facile method for synthesis of S-alkyl carbonothioates (1) through direct O-carbonylation of alcohols with carbon monoxide and sulfur in the presence of tertiary amine (eq. 1).⁴⁾ Best results were obtained when DBU (1,8-diazabicyclo[5.4.0]-7-undecene) was employed as a tertiary amine.⁵⁾ To the best of our knowledge, this is the first example of sulfur-assisted O-carbonylation of alcohols with carbon monoxide.

$$ROH + CO + S \xrightarrow{DBU} ROCS^{-}(DBU \cdot H)^{+} \xrightarrow{R'X} ROCSR' (1)$$

$$2 \qquad 1$$

The typical procedure is as follows: in a 100mL stainless steel autoclave, n-butanol (0.46 mL, 5 mmol), powdered sulfur (0.48 g, 15 mmol), DBU (3.7 mL, 25 mmol), and THF (10 mL) are placed with a magnetic stirring bar under nitrogen atmosphere. The autoclave is then flushed several times with carbon monoxide and finally charged with carbon monoxide at 30 kg/cm² at room temperature. The reaction is carried out at 80°C for 4 h with vigorous stirring. After the reaction, subsequent esterification of 2 with benzyl bromide (0.71 mL, 6 mmol) under ordinary pressure followed by fractional distillation gave 0.96 g of S-benzyl O-n-butylcarbonothioate (86 % yield, based on n-butanol used).

Various S-alkyl carbonothioates (1) were prepared selectively in good to excellent yields under the similar reaction conditions (Table 1). This reaction could be also applied to secondary and tertiary alcohols successfully.

alcohol	alkyl halide	product	yield,% ^a
n-BuOH	PhCH ₂ Br	n-BuOC(O)SCH ₂ Ph	86
	CH2=CHCH2Br	n-BuOC(0)SCH ₂ CH=CH ₂	100
	n-BuI	n-BuOC(O)SBu-n	75
MeOH	PhCH ₂ Br	MeOC(O)SCH ₂ Ph	74
EtOH	PhCH ₂ Br	EtOC(O)SCH ₂ Ph	93
n-PrOH	PhCH ₂ Br	n-PrOC(O)SCH ₂ Ph	86
iso-PrOH	PhCH ₂ Br	iso-PrOC(O)SCH ₂ Ph	82
^{n-C} 10 ^H 21 ^{OH}	PhCH ₂ Br	$n-C_{10}H_{21}OC(0)SCH_2Ph$	81
PhCH ₂ OH	PhCH ₂ Br	PhCH ₂ OC(O)SCH ₂ Ph	83
CH2=CHCH2OH	PhCH ₂ Br	$CH_2 = CHCH_2OC(O)SCH_2Ph$	71
сн ₃ осн ₂ сн ₂ он	PhCH ₂ Br	CH3OCH2CH2OC(0)SCH2Ph	87
tert-BuOH	PhCH ₂ Br	tert-BuOC(O)SCH ₂ Ph	52

Table 1 Various S-Alkyl Carbonothioates (1) Synthesis

^aIsolated yields based on alcohol used.

From a viewpoint of the simple operation and good to excellent yields, the present reaction may be considerably convenient method for synthesis of Salkyl carbonothioates (1).

References and Notes

- 1) R. A. Franz and F. Applegath, J.Org.Chem., 26,3304,3306,3309(1961).
- D. W. Grisley, Jr. and J. A. Stephens, J.Org.Chem., 26,3568(1961).
 T. Mizuno, I. Nishiguchi, T. Hirashima, A. Ogawa, N. Kambe, and N.Sonoda, Synthesis, 1988,257.
- 4) S-Alkyl carbonothicates 1 can be obtained by the reaction of alcohols with carbon oxide sulfide and alkyl halide. Carbon oxide sulfide is usually produced from carbon monoxide and melted sulfur at considerably high temperature (250-450°C), for a review, see: K. Mori, M. Shimizu, and T. Kanazawa, J.Synth.Org.Chem., Japan, 29,609(1971).
- 5) Effect of various bases for this carbonylation was also investigated, DBU; 99 %, DBN (1,5-diazabicyclo[4.3.0]-5-nonene); 54 %, Et₃N; 68 %, n-Bu₃N; 5 %, N-methylpyrrolidine; 13 %, pyridine; 0 %, N,N-dimethylaniline; 0 %, K_2CO_3 ; 9 %, NaOH; 0 % (GLC yields of S-benzyl O-n-butylcarbonothioate).

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