

$\text{Me}_3\text{SiSSiMe}_3$ (99.7 mg, 0.56 mmol) in 0.5 mL of CH_3CN led to an exothermic reaction, which was monitored by GC/MS analysis. Upon completion, the reaction mixture is directly poured onto a chromatographic column packed with Florisil, under inert atmosphere, and eluted with hexane. The blue fraction is collected, and the solvent is removed at room temperature under vacuum to afford a blue oily residue.⁷

Several representative examples are summarized in Table I. The above reaction could also be successfully applied to aldehydes: the mildness of our method, in this case, allows the in situ formation of the thioaldehydes⁸ in the monomeric form, which can be trapped with dienes, leading for example to cycloadducts **3a-c** (Scheme II) in very high yields.⁹

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ proved in our hands to be the most effective and mild catalyst, with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ leading to a more extended degree of oligomerization in the case of aliphatic and aromatic compounds (**1a-f**) and to complete polymerization in the case of furoyl- and thenoyltrimethylsilane and of aldehydes. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ proved, on the other hand, to be ineffective.

However ketones, such as acetophenone and benzophenone, when treated under the conditions of scheme I,

(7) $^1\text{H NMR}$ (CDCl_3) δ 0.38 (s, 9 H), 6.82-8.20 (m, 5 H). MS: *m/e* (relative intensity) 194 (M^+ , 30), 179 (57), 135 (45), 121 (31), 104 (61), 77 (22), 73 (100). λ_{max} (Et_2O): 678 (ϵ 38).

(8) Reactions between aldehydes and organosilathianes have been reported: (a) Lebedev, E. P.; Mizhiritskii, M. D.; Baburina, V. A.; Zariipov, Sh. I. *Zh. Obshch. Khim.* 1979, 49, 1084; *Chem. Abstr.* 1979, 91, 39578y. (b) Segi, M.; Nakajima, T.; Suga, S.; Murai, S.; Ryu, I.; Ogawa, A.; Sonoda, N. *J. Am. Chem. Soc.* 1988, 110, 1976 and references cited therein.

(9) General experimental procedure: a solution of benzaldehyde (50 mg, 0.47 mmol), 2,3-dimethylbutadiene (57.4 mg, 0.70 mmol), and hexamethyldisilathiane (83.7 mg, 0.47 mmol) in 0.5 mL of CH_3CN (RPE Carlo Erba) was treated with a solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (22 mg, 0.094 mmol) in 1 mL of CH_3CN . The reaction mixture was stirred overnight, quenched with 5% NaHCO_3 , extracted with ether, and eluted on silica gel to obtain 84.5 mg (88%) of compound **3c**. $^1\text{H NMR}$ (CDCl_3): δ 1.73 (s, 3 H), 1.75 (s, 3 H), 2.53 (broad d, 2 H, $J = 6$ Hz), 2.93 (broad d, 1 H, $J = 16.8$ Hz), 3.29 (broad d, 1 H, $J = 16.8$ Hz), 4.11 (t, 1 H, $J = 6.6$ Hz), 6.15 (m, 1 H), 6.32 (m, 1 H), 6.62 (m, 1 H) ppm. MS: *m/e* (relative intensity) 194 (M^+ , 68), 126 (7), 113 (21), 112 (100), 67 (11).

failed to afford the desired thio derivatives, showing this reaction, at least in this first stage, to be limited to the much more reactive acylsilanes and aldehydes.

Although group 14 organometallic sulfides have already been used for the formation of thiocarbonyl derivatives, our method offers several advantages and complements those previously reported. In fact, while Steliou's method¹⁰ appears to be successful with ketones, it leads to lower yields for acylsilanes and affords isolation only of the trimers of thioaldehydes. On the other hand, the very recent procedure^{8b} based on the *n*-BuLi-catalyzed addition of $\text{Me}_3\text{SiSSiMe}_3$ to aldehydes does not appear to work at all when applied to acylsilanes.

Further synthetic applications of this new method are currently being investigated in our laboratory.

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Registry No. **1a**, 13411-48-8; **1b**, 82903-03-5; **1c**, 5908-41-8; **1e**, 68185-95-5; **1f**, 75748-09-3; **1g**, 80671-28-9; **1h**, 88372-95-6; **2a**, 117775-48-1; **2b**, 117775-49-2; **2c**, 79841-55-7; **2e**, 117775-50-5; **2f**, 117775-51-6; **2g**, 117775-52-7; **2h**, 117775-53-8; **3a**, 84040-18-6; **3b**, 117775-54-9; **3c**, 117775-55-0; PhCHO, 100-52-7; $(\text{Me}_3\text{Si})_2\text{S}$, 3385-94-2; $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 7646-79-9; $\text{H}_2\text{C}=\text{C}(\text{Me})\text{C}(\text{Me})=\text{CH}_2$, 513-81-5; 2-thienylformaldehyde, 98-03-3; 2-furylformaldehyde, 98-01-1.

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Regiospecific Carbonylation and Ring Expansion of Thietanes and Oxetanes Catalyzed by Cobalt and/or Ruthenium Carbonyls

Summary: Dicobalt octacarbonyl and triruthenium dodecacarbonyl together catalyze the regiospecific insertion of carbon monoxide into the least substituted carbon-heteroatom bond of a thietane or oxetane, affording thiobutyrolactones or butyrolactones in fine yields.

Sir: Metal complex catalyzed carbonylation reactions have been widely utilized in synthetic organic chemistry.^{2,3} An important class of carbonylation reactions are those that involve the direct incorporation of one or two molecules of carbon monoxide into a heterocyclic substrate resulting in ring expansion. This method has been particularly successful when applied to three-membered-ring heterocycles. Examples include the rhodium(I)-catalyzed monocarbonylation of 2-arylaziridines to 3-arylazetidines⁴ and the double carbonylation of styrene oxides to α -keto

lactones catalyzed by cobalt carbonyl under phase-transfer conditions.⁵ The reaction is regiospecific in both cases, with carbon monoxide insertion occurring into the most substituted carbon-heteroatom bond.

Little is known concerning the direct conversion of four- to five-membered-ring heterocycles by carbonylation. A patent⁶ describes the formation of γ -butyrolactone in 55% yield when oxetane is subjected to cobalt acetate catalyzed carbonylation at 250 atm and 200 °C. We now report that such a transformation actually proceeds at considerably lower pressure. Of greater significance are the results of a study using substituted oxetanes and thietanes, which demonstrates the regio- and stereospecificity of the reaction. An added feature, especially for thietanes, is the use of both ruthenium and cobalt carbonyls as catalysts in order to realize the formation of products in high yields.

Treatment of oxetane with carbon monoxide and a catalytic quantity of cobalt carbonyl [10:1 molar ratio of

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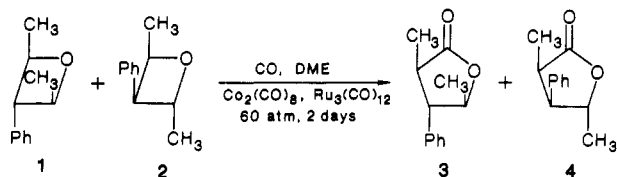
Table I. Metal-Catalyzed Carbonylation of Oxetanes and Thietanes

substrate	Co ₂ (CO) ₈ ^a	Ru ₃ (CO) ₁₂ ^a	temp, °C	product ^b	yield, %
oxetane	yes	no	190	γ-butyrolactone	50
	no	yes			20
2-hexyloxetane ^c	yes	yes	165	4-hexylbutyrolactone	70
	no	yes			40
	yes	no			80
3,3-dimethyloxetane	yes	yes	165	3,3-dimethyl-γ-butyrolactone	89
	yes	yes			39
	yes	yes			63
3-(acetoxymethyl)-3-methyloxetane	yes	yes	240	3-(acetoxymethyl)-3-methyl-γ-butyrolactone	45
	yes	no			29
thietane	yes	no	125	γ-thiobutyrolactone	61
	no	yes			100
	yes	yes			95
2-methylthietane ^d	yes	yes	120	4-methyl-γ-thiobutyrolactone	95
3-methoxythietane	yes	yes	145	3-methoxy-γ-thiobutyrolactone	87

^aThe ratio of Co₂(CO)₈/Ru₃(CO)₁₂ was 1:1 when both were used as catalysts. ^bProducts were identified by comparison of spectral data [IR, NMR (¹H, ¹³C), MS] with literature values (where described) and with authentic materials. Satisfactory C, H analyses were obtained for new compounds. ^cOkuma, K.; Tanaka, Y.; Kaji, S.; Ohta, H. *J. Org. Chem.* 1983, 48, 5133. ^dLancaster, M.; Smith, D. J. H. *Synthesis* 1982, 582.

substrate:catalyst] in 1,2-dimethoxyethane (DME), for 2 days at 190 °C and 60 atm, affords γ-butyrolactone in 50% yield. The yield is only 20% when triruthenium dodecacarbonyl is employed as the catalyst. However, use of equimolar amounts of both metal carbonyls as catalysts [i.e. 10–20:1:1 molar ratios of substrate:Co₂(CO)₈:Ru₃(CO)₁₂] results in formation of the lactone in 70% yield. Inferior results are obtained by using other ratios of Co₂(CO)₈/Ru₃(CO)₁₂ [i.e. 1:2 (20% yield), 2:1 (30%)].

When thietanes are compared with oxetanes, the contrast in catalytic activity of cobalt and ruthenium carbonyls is intriguing; ruthenium carbonyl is a superior catalyst to cobalt for thietane while the reverse is true for oxetane. However, together Ru₃(CO)₁₂ and Co₂(CO)₈ are an excellent catalytic system for thietane and substituted analogues (Table I). Thietanes are also more reactive than oxetanes with lower temperatures required for the sulfur compounds. The ring expansion process is regiospecific for both classes of heterocycles [i.e., 2-hexyloxetane, 2-methylthietane] with carbonyl insertion occurring into the least substituted of the two carbon-heteroatom bonds. Furthermore, the process proceeds with retention of substituent group stereochemistry. A 3.31/1.00 mixture (NMR analysis) of 1/2, obtained from *trans*-1-phenylpropene and acetaldehyde,⁷ affords 3/4 in a 3.28/1.00 ratio (NMR) on Co₂(CO)₈/Ru₃(CO)₁₂-catalyzed carbonylation.



The following general procedure was used: a mixture of the oxetane or thietane [2–4 mmol], Ru₃(CO)₁₂ [0.2

mmol], and Co₂(CO)₈ [0.2 mmol] in DME (10 mL) was heated for 2 days under 60 atm of carbon monoxide. The solution was cooled and filtered, and concentration of the filtrate gave the crude product. Pure lactone or thiolactone was obtained by silica gel thin layer chromatography using 2–4:1 hexane/methylene chloride as the developing solvent.

In conclusion, thiolactones and lactones can be synthesized by a regiospecific carbonylation of thietanes and oxetanes, respectively, using Co₂(CO)₈ and/or Ru₃(CO)₁₂ as the metal catalysts. In addition to being a simple route to these important classes of compounds, this process provides another illustration of the beneficial effect of using two metal complexes as homogeneous catalysts in a reaction.^{8,9}

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Registry No. 1, 73428-27-0; 2, 73466-20-3; 3, 117471-41-7; 4, 117471-42-8; Co₂(CO)₈, 15226-74-1; Ru₃(CO)₁₂, 15243-33-1; oxetane, 503-30-0; γ-butyrolactone, 96-48-0; 2-hexyloxetane, 74581-25-2; 4-hexylbutyrolactone, 706-14-9; 3,3-dimethyloxetane, 6921-35-3; 3,3-dimethyl-γ-butyrolactone, 3709-08-8; 3-(acetoxymethyl)-3-methyloxetane, 117471-37-1; 3-(acetoxymethyl)-3-methyl-γ-butyrolactone, 117471-39-3; thietane, 287-27-4; γ-thiobutyrolactone, 1003-10-7; 2-methylthietane, 17837-41-1; 4-methyl-γ-thiobutyrolactone, 117471-40-6; 3-methoxythietane, 117471-38-2; 3-methoxy-γ-thiobutyrolactone, 96862-65-6.

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Reduction of (*E,E*)-(η⁶:η⁶-1,4-Diphenyl-1,3-butadiene)bis(tricarbonylchromium), Followed by Reaction with Electrophiles. A Regioselective Method for the Preparation of Substituted 1,4-Diphenylbutenes

Summary: Reduction of (*E,E*)-(η⁶:η⁶-1,4-diphenyl-1,3-butadiene)bis(tricarbonylchromium) with lithium na-

phthalenide followed by reaction with alkyl halides and acyl chlorides yields, after oxidative cleavage of the tri-