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Preliminary communication

$Co_2(CO)_8$-mediated and -catalyzed carbonylation of diaryl diselenides and ditellurides to seleno and telluro esters

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Abstract

Diaryl diselenides and ditellurides react with CO (5–100 atm) at 100–200 °C in the presence of $Co_2(CO)_8$ to give the corresponding seleno and telluro esters in 21–96% yield. The carbonylation proceeds catalytically in $Co_2(CO)_8$ in the presence of triphenylphosphine. It was shown unambiguously that benzoylcobalt tetracarbonyl, which is one of possible intermediates, reacts with diphenyl diselenide or ditelluride to give phenyl selenobenzoate or tellurobenzoate, respectively.

Seleno- and telluro-carboxylic acid esters [1] are attractive compounds because they have liquid crystal properties [2], block certain nerve impulses [3], and can undergo degradation to nor-alkanes [4]. Several synthetic methods for their formation have been developed, which always use compounds bearing carbonyl groups such as RCOX or $RCOM^-$ (M = Se, Te) as starting substrates. The report [5] on $Co_2(CO)_8$-catalyzed carbonylation of diaryl disulfides to the corresponding thioesters prompted us to examine carbonylation of organic diselenides and ditellurides with CO so as to obtain seleno and telluro esters. Here we report our preliminary results of this approach.

The reaction conditions of $Co_2(CO)_8$-catalyzed carbonylation of disulfides were rather severe (185 °C/58 atm CO/ca. 24 h) and S–S bond fission was proposed for the first stage of the reaction. We presumed that the carbonylation of the corresponding diselenides and ditellurides might proceed under milder conditions as the Se–Se and Te–Te bonds are weaker than the S–S bond. We first compared the behaviour of each of the three diphenyldichalcogenides (**1a**, **1b**, **1c**) in regard to this carbonylation under relatively mild conditions (125 °C/10 atm CO/1 h). In acetonitrile with 40 mol% $Co_2(CO)_8$ phenyl thiobenzoate (**2a**) was scarcely formed, whereas phenyl selenobenzoate (**2b**) and tellurobenzoate (**2c**) were formed in 45 and 24% yields, respectively (see Table 1); diphenyl-mono-chalcogenides (**3a**–**3c**) were

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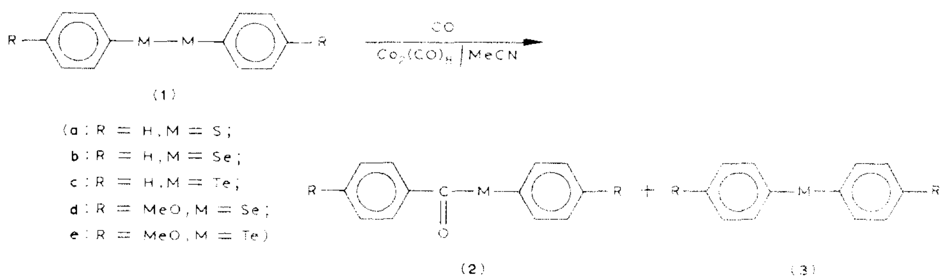
Table 1

Carbonylation of **1** with CO [a]

1 (1 mmol)	CO Pressure (atm)	$Co_2(CO)_8$ (mmol)	PPh_3 (mmol)	Tempe-rature (°C)	Products and yield (%) [b]	
1a	10	0.4		125	**2a**, trace	**3a**, trace
1b	10	0.4		125	**2b**, 45	**3b**, 1
1c	10	0.4		125	**2c**, 24	**3c**, 23
1b	100	0.4		200	**2b**, 96	**3b**, 2
1b	20	0.4		150	**2b**, 69	**3b**, 1
1b	5	0.4		150	**2b**, 23	**3b**, 2
1d	20	0.4		150	**2d**, 49	**3d**, 3
1c	100	0.4		125	**2c**, 40	**3c**, 7
1e	20	0.4		125	**2e**, 7 [c]	**3e**, 19 [c]
1b	100	0.01	0.5	200	**2b**, 20	**3b**, 0
1b	100	0.1	1.0	200	**2b**, 78	**3b**, 2
1b	10	0.1	0.5	150	**2b**, 48	**3b**, trace

[a] In acetonitrile (5 ml), in a stainless steel autoclave with teflon container, for 1h. [b] Determined by GLC and based on amount of **1** charged. [c] Isolated yield.



obtained as by-products. In benzene as solvent the yields of the ester fall in the order Te > Se > S. These facts support the assumption that the reaction starts with M–M bond fission.

To determine the optimum conditions for the preparation of **2b** and **2c**, compound **1b** was treated with CO (5–100 atm) in acetonitrile in the presence or absence of various metal compounds (5–100 mol%) at 100–200 °C for 1–12 h. Of the metal compounds examined, $Co_2(CO)_8$ gave the best results, with $Co(OAc)_2 \cdot 4H_2O$, $Mn_2(CO)_{10}$ and $Pd(PPh_3)_4$ being only slightly effective, whereas compounds such as $Mo(CO)_6$, $Mn(CO)_5Br$, $Rh_6(CO)_{16}$, $RuCl_3$, $CoCl_2 \cdot 6H_2O$, Li_2PdCl_4, $PtCl_2$ and $H_2PtCl_6 \cdot 6H_2O$ were ineffective. The yield of **2b**, which increased with increase in the amount of $Co_2(CO)_8$ and with shorter reaction times, was almost quantitative when the reaction was carried out at 200 °C at 100 atm CO for 1 h using 40 mol% of $Co_2(CO)_8$. The reactivity of the selenide **1d** was less than that of **1b**. The preparation of the telluro esters **2c** and **2e** from the tellurides **1c** and **1e** required lower temperatures and shorter reaction times because of the instability of the esters formed. Typical results are shown in Table 1 *.

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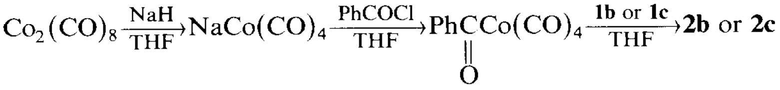
* All selenides, tellurides, and their products are known compounds except for **2d** (m.p. 111–113 °C) and **2e** (m.p. 172–174 °C), which gave satisfactory combustion analytical and spectroscopic data (^1H NMR and IR).

In contrast to the disulfide [5], the carbonylation of **1b** did not proceed catalytically in $Co_2(CO)_8$, under the above conditions, until triphenylphosphine had been added to the reaction system (see Table 1). This is probably because elemental Se, probably formed from SeCO during the reaction, is trapped by the phosphine instead of deactivating the catalyst. In fact, a separate experiment in the presence of an equimolar (to **1b**) amount of added Se powder, resulted in a decrease in yield of **2b** to about 50% of that obtained without the addition of Se. Triphenylphosphine reacts readily with Se to give triphenylphosphine selenide [6].

Although the details of the reaction are not yet clear, the following observations are noteworthy. Benzoylcobalt tetracarbonyl prepared in situ [7] reacts readily with **1b** and **1c** in tetrahydrofuran to give **2b** and **2c**; i.e., even at 20 °C under 1 atm of CO, **2b** or **2c** is obtained in 45 or 32% yield, respectively.



$$Co_2(CO)_8 \xrightarrow[\mathrm{THF}]{\mathrm{NaH}} NaCo(CO)_4 \xrightarrow[\mathrm{THF}]{\mathrm{PhCOCl}} \mathrm{Ph}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{Co(CO)_4} \xrightarrow[\mathrm{THF}]{\mathbf{1b}\ \mathrm{or}\ \mathbf{1c}} \mathbf{2b}\ \mathrm{or}\ \mathbf{2c}$$

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