

A Facile Insertion of Carbon Monoxide into C–Te Bonds of Organotellurium(II) and (IV) Compounds leading to Carboxylic Acids

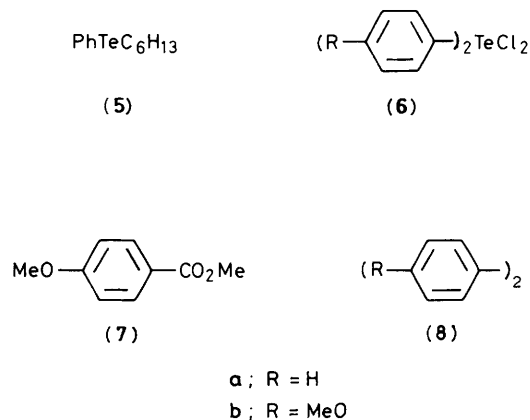
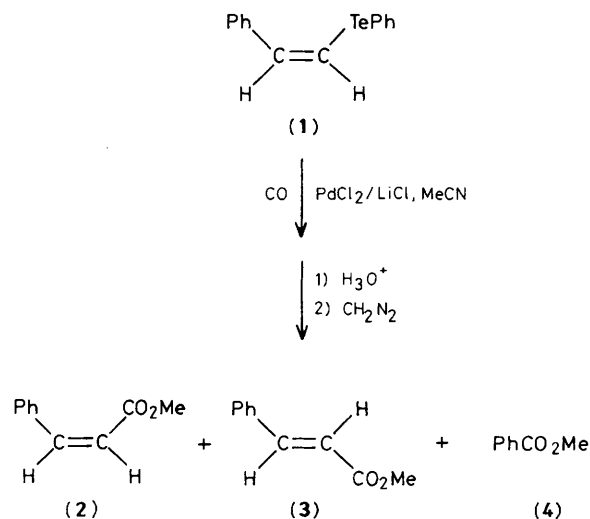
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Treatment of some organotellurium(II) and (IV) compounds with CO in the presence of PdCl₂ and LiCl gives aryl and vinylic carboxylic acids in good to high yields; in the case of (*Z*)-PhCH=CHTePh the major product was *cis*-cinnamic acid at 5–50 atm CO and the *trans*-isomer at 1 atm CO respectively.

The organic chemistry of tellurium is of current interest.¹ This communication reports the first facile insertion of carbon monoxide into C–Te bonds of organotellurium(II) and (IV) compounds leading to the corresponding carboxylic acids in the presence of palladium(II) salts. This is a characteristic reaction of tellurium among the group 6B elements, since the corresponding organo-sulphur and -selenium compounds did not afford any carbonylation products under similar conditions. The only example of carbonylation of organotellurium compounds so far known is the reaction of aryltellurium(IV) chlorides with Ni(CO)₄ under drastic conditions.²

Treatment of (*Z*)-phenyl styryl telluride (1)³ with CO at atmospheric pressure and at room temperature for 1.5 h in the presence of palladium(II) chloride [equimolar to (1)] and lithium chloride afforded *cis*- and *trans*-cinnamic acids in high yields (*trans* rich) together with benzoic acid and minor amounts of stilbenes and biphenyl. Ketones and aldehydes such as benzophenone, benzalacetophenone, dibenzalacetone, cinnamaldehyde, and benzaldehyde were not detected in the products. The isomer ratios were determined by g.l.c. as their methyl esters, (2)–(4), on treatment with diazomethane. The yields of (2) and (3) and the isomer ratio were unchanged by prolonging the reaction time to 20 h or by use of 2 mol equiv. PdCl₂, only an increase in (4) being observed in the latter case. In the absence of LiCl, however, (3) became almost the sole product. Interestingly, when the reaction was



carried out at a higher pressure of CO, the *cis*-isomer (2) became the major product irrespective of the reaction time and the pressure (5–50 atm). The difference in the dissolved CO concentration could be one reason for the change of isomer distribution, although the details are not yet known. From *n*-hexyl phenyl telluride (5), only (4) was obtained in a good yield and no *n*-heptanoic acid was formed.

Similar treatment of diphenyltellurium dichloride (6a) and bis(4-methoxyphenyl)tellurium dichloride (6b) with 1 atm CO afforded the corresponding carboxylic acid methyl esters, (4)

Table 1. Carbonylation of some organotellurium compounds with CO.^a

Te Compound 1 mmol	CO Pressure/ atm	Time/h	Products; % yield ^b					
(1)	1	1.5	(2)	32	(3)	52	(4)	8
(1)	1	20	(2)	28	(3)	55	(4)	10
(1) ^c	1	20	(2)	30	(3)	50	(4)	45
(1) ^d	1	20	(2)	3	(3)	60	(4)	4
(1)	5	1.5	(2)	34	(3)	21	(4)	4
(1)	20	1.5	(2)	46	(3)	22	(4)	5
(1)	50	1.5	(2)	69	(3)	16	(4)	7
(5)	1	20	(4)	73	(8a)	3		
(6a) ^c	1	20	(4)	42 ^e	(8a)	27		
(6a) ^c	20	20	(4)	63 ^e	(8a)	6		
(6b) ^c	1	20	(7)	36 ^e	(8b)	57		
(6b) ^c	20	20	(7)	41 ^e	(8b)	11		

^a Carried out in acetonitrile (7–10 ml) at 20–30 °C using PdCl₂ (1 mmol)/LiCl (2 mmol). A normal glass flask (1 atm CO) and a stainless steel autoclave with a glass container (5–50 atm CO) were used.

^b Determined by g.l.c.; 1 mmol corresponds to 100%. ^c PdCl₂(2 mmol)/LiCl(4 mmol). ^d PdCl₂(1 mmol). ^e 2 mmol corresponds to 100%.

and (7), together with aromatic coupling compounds, (8a) and (8b), respectively. The reaction at higher pressure of CO resulted in an increase in the yield of carboxylic acid by suppressing the formation of (8). Diphenyl telluride behaved similarly to (6a), while the reaction of 4-methoxyphenyltellurium trichloride gave mainly (8b) either at 1 atm or 20 atm CO. All reactions described above proceeded well in tetrahydrofuran or *N,N*-dimethylformamide as the solvent. These carbonylations did not occur at all in the absence of the palladium(II) salt even at 100 atm CO and 100 °C. Typical results are summarized in Table 1.

Since it is known that diaryl- or dialkyl-telluride forms complexes with transition metal halides including PdCl₂,⁴ i.e., (R₂Te)₂PdCl₂ and/or [(R₂Te)PdCl₂]₂ (R = aryl, vinyl, alkyl), the present carbonylation reaction may proceed *via* the formation of such complexes, in which the migration of R moiety from tellurium to palladium (transmetallation) occurs to give a reactive organopalladium species. An acylpalladium species is then formed by CO insertion followed by hydrolysis to carboxylic acid. The presence of such organopalladium species has been postulated in the olefin arylation and aromatic coupling in acetic acid as the solvent.⁵

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