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CARBODETELLURATION OF ARYLTELLURIUM(IV) COMPOUNDS: OLEFIN ARYLATION AND AROMATIC COUPLING

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Summary

Aryltellurium(IV) compounds react with olefins to give the corresponding arylated olefins in moderate to quantitative yield in the presence of a palladium(II) salt. The reaction proceeds catalytically with respect to the palladium(II) salt if a suitable oxidant, such as t-butyl hydroperoxide or copper(I) or (II) chloride, is added. In the absence of olefin the corresponding biaryls are formed in moderate yield. Transmetalation of tellurium with palladium is a key step of the reaction.

Introduction

Although there has been much activity in organotellurium chemistry [1], synthetically useful carbon—carbon bond formation using organotellurium compounds (carbodetelluration) seems to be so far limited to only two cases, namely, the synthesis of biaryls by Raney nickel reduction of diaryltellurium(IV) dichlorides [2] and the carbonylation of aryltellurium(IV) chlorides with $Ni(CO)_4$ [3]. It should be worthwhile to find further methods for the utilization of organotellurium(IV) compounds in synthesis, since these are easily prepared [2]. We have found [4] that several aryltellurium(IV) compounds react with olefins to give the corresponding arylated olefins in the presence of palladium(II) species and that they gave biaryls when olefin is absent. The olefin arylation and biaryl formation observed here represent further examples of carbodetelluration. It is known that various arylmercury(II) [5] and arylthallium(III) compounds [6] and phenyl compounds of main Groups II, IV, V, and VI, such as PhMgX [7], Ph_4Sn [5], Ph_4Pb [5], Ar_3P [8], Ph_3As [9,10], Ph_3Sb [9,10], Ph_3Bi [9,10], Ph_2Se [10], and Ph_2Te [10] react with olefins in the presence of a palladium(II) salt to give aryl- or phenyl-substituted olefins.

TABLE 1

THE REACTION OF DIPHENYLTELLURIUM(IV) DICHLORIDE WITH OLEFINS IN THE PRESENCE OF VARIOUS METAL SALTS [a]

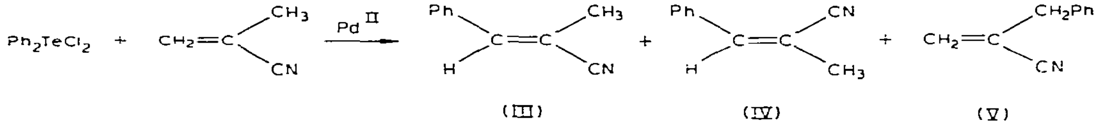
Olefin (10 mmol) R in I	Metal salt (mmol)					Solvent (20 ml)	Reaction time (h)	Product II and Yield (%) [b]
	$PdCl_2$	Pd black	NaOAc	LiCl	K_2CO_3			
Ph	2		4			AcOH	1	54 [c]
Ph		2	4			MeOH	1	34
Ph	2			4	2	MeCN	3	50
Ph [d]	$RuCl_3 3H_2O$ 1		3			AcOH	1	29
Ph [d]	$RhCl_3 3H_2O$ 1		3			AcOH	1	8
CO_2Me	2		4			AcOH	3	41
CO_2Et		2	4			AcOH	1	8
CN	2		4			AcOH	1	47 (*trans*:*cis* = 74 : 26)
CN [d]	$Pd(OAc)_2$ 1					MeCN	7	28 (72 : 28)
$CH_2=C(CN)Me$ [e]	2		4			AcOH	1	46 [e]
CHO	2		4			AcOH	1	98
$COCH_3$	2		4			AcOH	1	47
CH_2OH	2		4			AcOH	1	$PhCH_2CH_2CHO$ 34 [f]
CH_2OAc	2		4			AcOH	1	24 [g]
CH_2Br	2		4			AcOH	3	$PhCH_2CH=CH_2$ 44

[a] Ph_2TeCl_2 (1 mmol), at reflux temperature. [b] Determined by GLC. The yield is based on eq. 1, 1 mole of Ph_2TeCl_2 corresponding to 2 mole of II. In almost all cases biphenyl (<3%) was formed. [c] Other products; biphenyl (6%) and 1-acetoxy-1-phenylethane (3.1 mmol). [d] Ph_2TeCl_2 (0.5 mmol), olefin (5 mmol), solvent (10 ml). [c] III : IV : V = 27 : 30 : 43, see text. [f] Other products; *trans*-$PhCH=CHCH_2OAc$ (8%) and $PhCH_2CH=CH_2$ (2%). [g] Other product; $PhCH_2CH=CH_2$ (2%).

Results and discussion

Treatment of diphenyltellurium(IV) dichloride and palladium(II) chloride-sodium acetate with styrene in acetic acid at reflux for 1 h afforded *trans*-stilbene (54% yield) and biphenyl (6% yield), together with 1-acetoxy-1-phenylethane which was formed by addition of acetic acid to styrene. Addition of sodium acetate was necessary in order to obtain a better yield of *trans*-stilbene. Similar reactions proceeded with palladium black, palladium(II) acetate, and ruthenium(III) and rhodium(III) chlorides in place of palladium(II) chloride, but the yields of the products were generally lower. The reaction was applicable to various olefins (I) such as acrylic esters, acrylonitrile, methacrylonitrile, acrylaldehyde, methyl vinyl ketone, and allylic alcohols and halides (eq. 1). In these cases the amount of acetic acid-olefin addition product was low, as expected. Typical results are summarized in Table 1. As shown in the table, olefin was usually used in a 10-fold excess with respect to diphenyltellurium(IV) dichloride. The reaction proceeded similarly in a 5-fold excess of olefin, though the yield of a side product, biphenyl, increased (vide infra). The stereochemistry of the phenylated olefins (II) was *trans* except for those derived from acrylonitrile and methacrylonitrile. From acrylonitrile a mixture of *trans*- and *cis*-cinnamonitriles (*trans* : *cis* = ca. 3 : 1) was obtained, while three products, as shown in eq. 2, were obtained from methacrylonitrile in a ratio of ca. 1 : 1 : 1.5 for III : IV : V.

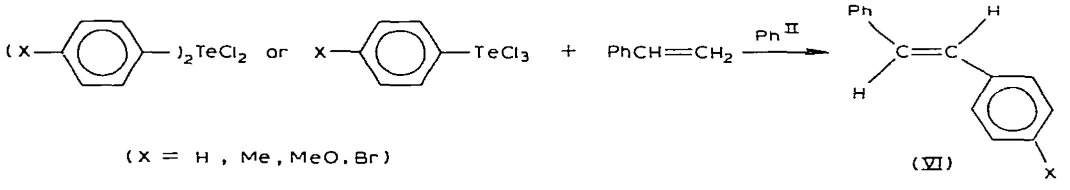
$$Ph_2TeCl_2 + \underset{(I)}{CH_2{=}CHR} \xrightarrow{Pd^{II}} \underset{(II)}{PhCH{=}CHR} \qquad (1)$$



(2)

In the cases of allyl alcohol and allyl bromide the main products were β-phenylpropionaldehyde and allylbenzene, respectively, as has been observed in the corresponding reactions with phenylmercury(II) compounds [11]. The reaction system using palladium(II) chloride-lithium chloride and potassium carbonate in acetonitrile also was found to be an effective one for the phenylation of styrene. Here, the addition of potassium carbonate was necessary to obtain a good yield of *trans*-stilbene.

Application of this arylation reaction to several *p*-substituted phenyltellurium(IV) compounds with styrene as substrate resulted in a formation of lower yields of the expected product (VI) than that of *trans*-stilbene in all cases examined (eq. 3). Typical results are shown in Table 2. The inorganic substituent (Cl vs. OAc) on tellurium in the phenyltellurium(IV) compounds did not affect the yield of *trans*-stilbene to a marked extent.



(3)

TABLE 2

ARYLATION OF STYRENE WITH VARIOUS ARYLTELLURIUM(IV) COMPOUNDS [a]

$ArTeCl_3$ (2 mmol) or Ar_2TeCl_2 (1 mmol)	$PdCl_2$ (mmol)	Additives (mmol)						Solvent (20 ml)	Reaction time (h)	Product and yield (%)	
		NaOAc	t-BuOOH	CuCl	$CuCl_2$	LiCl	K_2CO_3			VI	VII
Ph_2TeCl_2	2	4						AcOH	0.5	50	5
$Ph_2Te(OAc)_2$	2	4						AcOH	0.7	54	6
$PhTeCl_3$	2	4						AcOH	3	38	1
Ph_2TeCl_2	0.17	0.5	2					AcOH	1	32(370) [c]	3
Ph_2TeCl_2	0.17			1.7				AcOH	2.5	14(162) [c]	2
Ph_2TeCl_2	0.17				1.7			AcOH	2.5	35(413) [c]	1
p-$MeOC_6H_4TeCl_3$	2	4						AcOH	1	7	0
Ph_2TeCl_2	2					4	2	MeCN	3	50	3
p-$MeC_6H_4TeCl_3$	2					4	2	MeCN	3	26	6
p-$MeC_6H_4TeCl_3$	2					4		MeCN	3	3	trace
$(p$-$MeC_6H_4)_2TeCl_2$	2					4	2	MeCN	3	14	3
$(p$-$BrC_6H_4)_2TeCl_2$	2					4	2	MeCN	3	17	trace
$(p$-$MeOC_6H_4)_2TeCl_2$	2					4	2	MeCN	3	23	0
p-$MeOC_6H_4TeCl_3$	2					4	2	MeCN	3	4	0

[a] Styrene (10 mmol), at reflux temperature. [b] Determined by GLC. The yield is based on eqs. 3 and 4, 1 mole of Ar_2TeCl_2 corresponding to 2 mole of VI and 1 mole of VII. Also 1 mole of $ArTeCl_3$ to 1 mole of the former and 0.5 mole of the latter. [c] Based on $PdCl_2$ charged.

TABLE 3

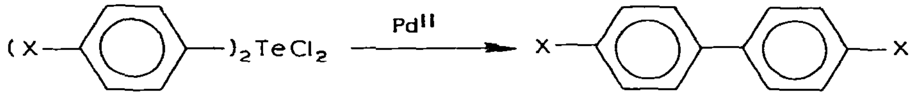
AROMATIC COUPLING OF ARYLTELLURIUM(IV) COMPOUNDS [a]

Ar_2TeCl_2 or $ArTeCl_3$ (1 mmol)	Reaction time (h)	Product VII	Yield (%) [b]
Ph_2TeCl_2	1	X = H	35
$(p\text{-}MeC_6H_4)_2TeCl_2$	1	X = Me	51
$(p\text{-}BrC_6H_4)_2TeCl_2$	1	X = Br	40
$(p\text{-}MeOC_6H_4)_2TeCl_2$	1.5	X = MeO	10
$p\text{-}MeOC_6H_4TeCl_3$ [c]	5	X = MeO	3

[a] $PdCl_2$ (2 mmol), NaOAc (4 mmol), AcOH (20 ml), at reflux. [b] Determined by GLC. The yield is based on eq. 4, 1 mole of Ar_2TeCl_2 corresponding to 2 mole of VII. [c] $PdCl_2$ (1 mmol) and NaOAc (2 mmol) were used in this case.

The reaction was found to be catalytic in palladium(II) chloride if a suitable oxidant was added to the reaction system, t-butyl hydroperoxide or copper(II) chloride being especially effective in acetic acid solution. In acetonitrile, on the other hand, t-butyl hydroperoxide did not show any effect on the catalytic cycle.

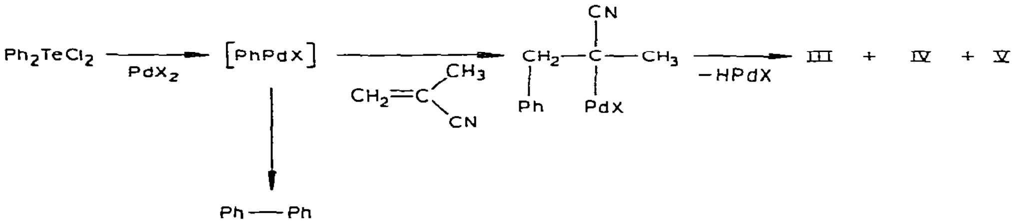
In this arylation reaction a small amount of biaryl always was formed. When a similar reaction was carried out without the addition of olefin, the biaryl (VII) became the sole product in moderate yield (Table 3) (eq. 4).



(4)

(VII)

Considering the kind of products and the isomer ratios, it is reasonable to assume that this carbodetelluration involves a reactive arylpalladium(II) species, as has been postulated by Heck [5,11] in the reactions with arylmercury(II) compounds. Tellurium(IV)—palladium(II) exchange occurs as a first step to give the arylpalladium(II) species which adds to C=C double bond. This is followed by elimination of vicinal hydrogen (or bromine in the case of allyl bromide) and palladium(II). Alternatively, coupling to give the biaryl occurs in the absence of olefin. Thus, the formation of three products from methacrylonitrile can be understood as shown in eq. 5. We have observed separately that



(5)

similar reactions with phenylmercury(II) chloride or phenylthallium(III) bis(trichloroacetate) gave also a mixture of III, IV, and V in about 60% yield, the isomer ratio being close to that obtained in tellurium(IV) case [12]. This result may be indicative of the presence of essentially the same reactive species in these three reactions. Our finding described here appears to be the first example of transmetalation of tellurium(IV) with palladium(II).

Experimental

^{1}H NMR spectra were recorded with a Varian EM-360 (60 MHz) spectrometer in $CDCl_3$ or CCl_4. GLC analyses were carried out using a Shimadzu 4CMPF apparatus using EGSS-X (15%) -Chromosorb-W (1 or 3 m) and Apiezon-L (1 m) columns (N_2 as carrier gas). Commercially available organic and inorganic compounds were used without further purification. Diaryltellurium dichlorides were prepared by the reaction of $TeCl_4$ with the corresponding aromatics [2] or by the reaction of tellurium metal with the corresponding diazonium salt [13]. Phenyltellurium trichloride was prepared from benzene, $TeCl_4$, and $AlCl_3$ [14] or, more conveniently, by the reaction of phenylmercury(II) chloride with $TeCl_4$ in dioxane [15]. *p*-Tolyltellurium trichloride was prepared by stirring toluene (40 ml) and $TeCl_4$ (7 g) at reflux for 20 h, collecting the white precipitate, and washing with CCl_4: yield 7 g (83%), m.p. 178—179°C (lit. [15] m.p. 181—182°C). *p*-Anisyltellurium trichloride was prepared by heating a mixture of anisole and $TeCl_4$ at 70°C for 1 h [2]. Diphenyltellurium diacetate was prepared by reaction of the corresponding dichloride with silver acetate in dioxane at reflux for 4 h [16,17]. Authentic samples such as arylated olefins and biaryls for GLC analysis were commercial products or were prepared by similar treatment of the corresponding arylmercury(II) [5,11] or arylthallium(III) compounds [6,18]. A typical experimental procedure is given below.

Reaction of p-tolyltellurium(IV) trichloride with styrene in acetonitrile

A mixture of *p*-tolyltellurium(IV) trichloride (0.325 g, 1 mmol), styrene (1.04 g, 10 mmol), palladium chloride (0.355 g, 2 mmol), lithium chloride (0.17 g, 4 mmol), and potassium carbonate (0.276 g, 2 mmol) in acetonitrile (20 ml) was heated at reflux for 3 h under stirring. After the mixture had been cooled to room temperature, the precipitated black solid was filtered and the red filtrate was treated with aqueous NaCl and extracted with chloroform. The extracts were dried over $MgSO_4$. GLC analysis showed the presence of *trans-p*-methylstilbene (0.254 mmol, 25.4%) and 4,4'-ditolyl (0.03 mmol, 6.0%) (ethyl cinnamate as internal standard).

Reaction of diphenyltellurium(IV) dichloride with styrene in the presence of a catalytic amount of palladium(II) chloride

A mixture of diphenyltellurium(IV) dichloride (0.35 g, 1 mmol), styrene (1.04 g, 10 mmol), palladium(II) chloride (0.03 g, 0.17 mmol), and copper(II) chloride (0.23 g, 1.7 mmol) in acetic acid (20 ml) was heated at reflux for 2.5 h with stirring. After the mixture had been cooled to room temperature, the black precipitate (ca. 0.01 g) was filtered and the pale green filtrate was treated with aqueous NaCl (200 ml) and extracted with benzene. The extracts were washed with aqueous $NaHCO_3$ and then with aq. NaCl and dried over Na_2SO_4. GLC analysis using ethyl cinnamate as internal standard showed the presence of *trans*-stilbene (0.702 mmol; 35.1% based on Ph_2TeCl_2, 413% based on $PdCl_2$) and very small amounts of biphenyl and unidentified compounds.

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