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PHOSPHINE-NICKEL(II), -COBALT(II), -PALLADIUM(0) AND -PALLADIUM(II) COMPLEXES AS CATALYSTS IN CROSS-COUPLING REACTIONS OF ARYL- AND ALKYL-GRIGNARD REAGENTS WITH ORGANIC TELLURIDES

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Summary

Some alkyl- and aryl-tellurides react with Grignard reagents (RMgBr; R = aryl and alkyl) in the presence of $NiCl_2(PPh_3)_2$, $NiCl_2(Ph_2PCH_2CH_2CH_2PPh_2)$, or $CoCl_2(PPh_3)_2$ as catalyst in THF or diethyl ether as solvent to give the cross-coupling products together with the homo-coupling products of the tellurides in good to moderate yields, with elemental tellurium being formed as a black precipitate. A catalytic reduction-oxidation cycle involving a Ni or Co complex bearing an organotellurium moiety (RTe; R = alkenyl, aryl, and alkyl) is proposed for the reaction. Palladium catalysts such as $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, and $PdCl_2(PhCN)_2$ are revealed to be much less effective than the Ni and Co catalysts in both the yield and the stereoselectivity of the product.

Introduction

In the synthetic reactions known using organotellurium compounds and tellurium salts [1], useful carbon–carbon bond-formation reactions seem to be still limited to date; i.e., Raney nickel reduction [2], a thermal decomposition [3,4], $Ni(CO)_4$ insertion [5], Pd transmetallation [6,7], and Te^{2-}-induced allylic coupling [8]. Since many organotellurium compounds are stable and easily prepared [9], it is desirable to find further methods of C–C bond formation for the utilization of these compounds in organic synthesis. As one of our series of studies on the substitution of the tellurium moiety of organotellurium compounds by several functional groups [6,10], we report here a first example of Ni^{II} and Co^{II}-phosphine complex-catalyzed cross-coupling reaction between Grignard reagents and readily accessible organic tellurides and organotellurium(IV) halides [11]. To our knowledge, there are no reports on such transition metal-catalyzed cross-coupling reactions by use of organotellurium compounds, although similar reactions using Ni-phosphine complex

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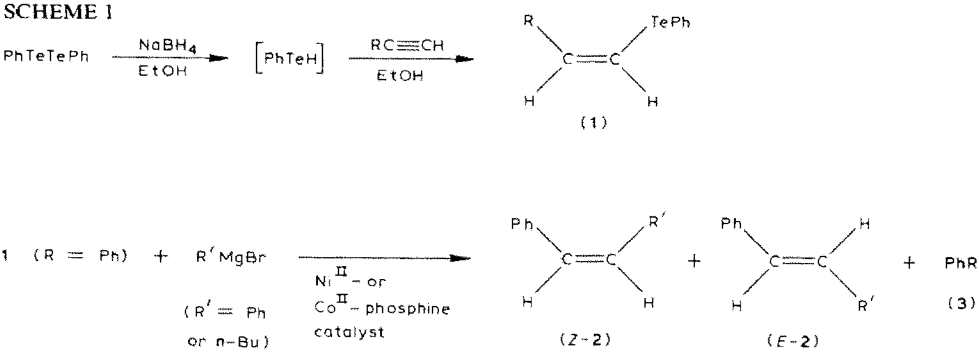
catalysts have been reported on organic halides [12,13], ethers [14], sulfides [15,16], and selenides [17].

Results and discussion

When (*Z*)-phenyl styryl telluride (**1**; R = Ph) (1 equiv.), prepared by stereospecific *trans*-addition of phenyltellurol to phenylacetylene, was treated with phenylmagnesium bromide (2.5 equiv.) in the presence of a catalytic amount of $NiCl_2(PPh_3)_2$ (0.05 equiv.) in tetrahydrofuran (THF) at 20°C for 10 min under nitrogen atmosphere, stilbene (60% yield, *cis/trans* = 9/1) and biphenyl were obtained as products (Scheme 1; R′ = Ph). Elemental tellurium was deposited as a black precipitate. A similar reaction at reflux temperature generally improved both the yield and the *cis*-selectivity of stilbene; i.e., for 3 h the yield and its isomer ratio were 100% and 98/2 (*cis/trans*), respectively. The use of more or less than 0.05 equiv. of the Ni catalyst resulted in lower yield and/or *cis*-selectivity of stilbene. The corresponding Co^{II} catalyst, $[CoCl_2(PPh_3)_2]$, and $NiCl_2(Ph_2PCH_2CH_2CH_2PPh_2)$ were revealed to be also effective for this coupling reaction, the selectivity for *cis*-stilbene and its yield being nearly the same as in the case of $NiCl_2(PPh_3)_2$. The reaction proceeded similarly in diethyl ether as solvent. The reaction of **1** (R = Ph) with BuMgBr was sluggish and gave much lower yields of the corresponding coupling products [**2** and **3**; R′ = Bu] when either the Ni^{II}- or Co^{II}- phosphine complex was used in THF or diethyl ether. Here, stilbene **2** (R′ = Ph) (*Z/E* = 100/0) was also formed, showing the occurrence of formal detelluration from **1** (R = Ph). The isomer ratio of *Z*- to *E*-**2** is kinetically controlled, since it was separately confirmed that isomerization between both isomers hardly occurred under the present reaction conditions. It was also confirmed that even in the absence of **1** (R = Ph) the homo-coupling of PhMgBr itself and the cross-coupling of that with bromobenzene (a small amount) left in the Grignard reagent occur to give a considerable amount of biphenyl in either THF or diethyl ether under our reaction conditions. Moreover, the freshly prepared Grignard reagent solution already contained biphenyl (see Experimental). Therefore, the amount of biphenyl **3** (R′ = Ph) formed in the reaction shown in Scheme 1 should be the sum of all these and that from the cross-coupling between **1** (R = Ph) and PhMgBr. Typical results are summarized in Table 1.

SCHEME 1



A similar coupling reaction occurred when using either the Pd^{II}- or Pd^{0}- com-

TABLE 1

CROSS-COUPLING BETWEEN **1** (R = Ph) AND GRIGNARD REAGENTS (R'MgBr)[a]

R' (2.5 mmol)	Catalyst[b] (0.05 mmol)	Solvent (10 ml)	Reaction temp. (°C)	Reaction time (h)	Product and yield (mmol)[c]			
					2	(*Z*:*E*)	**3**	PhTePh
Ph	A	THF	20	0.17	0.60	(90:10)	0.92	
Ph	A	THF	20	5	0.81	(97:3)	0.99	
Ph	A	THF	67	0.17	0.58	(96:4)	0.74	
Ph	A	THF	67	3	1.00	(98:2)	1.36	
Ph[d]	A	THF	67	3	–		0.88	
Ph[d]	A	THF	20	0.17	–		0.31	
Ph	A[e]	THF	20	5	0.51	(86:14)	0.24	
Ph	A[f]	THF	20	5	0.13	(100:0)	0.78	
Ph	A	Et_2O	20	5	0.64	(80:20)	0.80	
Ph	A	Et_2O	35	1	0.49	(90:10)	0.75	
Ph[d]	A	Et_2O	20	0.17	–		0.59	
Ph	B	THF	20	2	0.53	(100:0)	0.48	
Ph	B	Et_2O	35	1	0.76	(80:20)	1.00	
Ph	C	THF	20	5	1.00	(90:10)	1.04	
Bu	A	Et_2O	35	5	0.11	(85:15)	0.06[g]	
Bu	B	Et_2O	35	5	0.20	(80:20)	0.15[h]	
Bu	B	THF	67	3	0.15	(84:16)	0.10[i]	
Bu[d]	B	THF	67	3	–		–[j]	
Bu	C	Et_2O	35	5	0.12	(85:15)	0.04[g]	
Bu	C	THF	67	3	0.20	(80:20)	0.03[k]	
Ph	D	THF	25	0.17	0.05	(49:51)	0.05	0.07
Ph	D	THF	25	5	0.29	(69:31)	0.22	0.08
Ph	E	THF	25	0.17	0.13	(78:22)	0.12	0.03
Ph	E	THF	25	5	0.41	(75:25)	0.31	0.35
Ph	F	THF	25	0.17	0.04	(100:0)	0.13	0.06
Ph	F	THF	25	5	0.43	(87:13)	0.25	0.30

[a] Carried out using **1** (R = Ph) (1 mmol) under N_2. [b] A: $NiCl_2(PPh_3)_2$, B: $NiCl_2(Ph_2PCH_2CH_2CH_2PPh_2)$, C: $CoCl_2(PPh_3)_2$, D: $PdCl_2(PPh_3)_2$, E: $PdCl_2(PhCN)_2$, F: $Pd(PPh_3)_4$. [c] Determined by GLC. [d] Without **1** (R = Ph). [e] 0.1 mmol. [f] 0.025 mmol. [g] Small amounts of *cis*-stilbene and octane were also observed, but not determined. [h] Other products: *cis*-stilbene (0.05 mmol) and octane (0.11 mmol). [i] Other products: *cis*-stilbene (0.09 mmol) and octane (0.02 mmol). [j] Octane (0.05 mmol) was produced. [k] Other products: *cis*-stilbene (0.05 mmol) and octane (0.04 mmol).

plexes, but both the yield and the selectivity of the products were quite low. In these cases, the formation of diphenyl telluride was observed, and the amount of precipitated elemental tellurium was much less than that in the cases of Ni- and Co-complexes (Table 1).

Treatment of **1** (R = CO_2Et), prepared in the same manner as **1** (R = Ph), with PhMgBr in the presence of the Ni^{II}- or Co^{II}-phosphine complex (at 25°C for 5 h in THF) gave a very different result from the case of **1** (R = Ph); namely, the products are ethyl cinnamate, diphenyl telluride and biphenyl, with no trace of the corresponding *cis*-isomer and elemental tellurium being formed (Scheme 2). The formation of diphenyl telluride was observed even without the addition of the catalyst, the same phenomenon being also observed in the case of **1** (R = Ph). The results are shown in Table 2.

TABLE 2

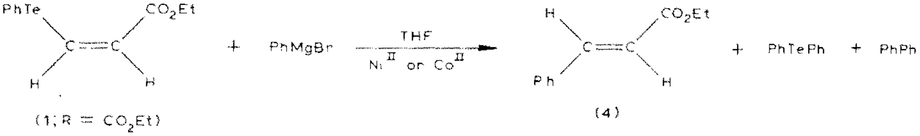
CROSS-COUPLING BETWEEN **1** (R = CO_2Et) AND PhMgBr[a]

Catalyst[b] (0.05 mmol)	Product and yield (mmol)[c]		
	4	PhTePh	PhPh
A	0.28	0.38	0.38
C	0.18	0.18	0.39
–	0.02	0.35	0.01

[a] Carried out using **1** (R = CO_2Et) (1 mmol), PhMgBr (2.5 mmol) and THF (10 ml) under N_2 at 25°C for 5 h. [b] See footnote of Table 1. [c] Determined by GLC.

Application of the reaction to a diaryl telluride (**5**) resulted in the formation of a mixture of the cross-coupling product (**6**) between both reagents and the homo-coupling products of each reagent (**7** and **8**) (Scheme 3) where **6** was mainly formed in the case of R = aryl. The organic moiety of the Grignard reagent replaced the tellurium group of **5** selectively at the *ipso*-position. During the reaction black elemental tellurium was deposited. The reaction was sluggish when R = hexyl and a major product was the homo-coupled dodecane **8** (R = hexyl) in many cases. Hexyl phenyl telluride similarly reacted with RMgBr to give the expected products. Typical results are summarized in Table 3. We have confirmed separately that all these coupling reactions proceed extremely slowly in the absence of a Ni^{II}- or Co^{II}-phosphine complex, and that **1** (R = Ph or CO_2Et) or **5** (Ar = *p*-$MeOC_6H_4$) by itself did not give any coupling products in the presence or absence of the $NiCl_2(PPh_3)_2$ catalyst in THF at reflux temperature.

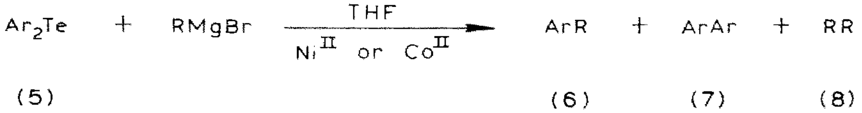
SCHEME 2



(1; R = CO_2Et)

(4)

SCHEME 3



$$\underset{(5)}{Ar_2Te} + RMgBr \xrightarrow[Ni^{II}\ \text{or}\ Co^{II}]{THF} \underset{(6)}{ArR} + \underset{(7)}{ArAr} + \underset{(8)}{RR}$$

The expected coupling products were also formed in the reaction using readily accessible aryltellurium(IV) compounds instead of diaryl telluride and alkyl aryl telluride (Table 3). For example, di-*p*-methoxyphenyltellurium dichloride reacted with PhMgBr in the presence of $NiCl_2(PPh_3)_2$ to give the expected 4-methoxybiphenyl and 4,4′-dimethoxybiphenyl in reasonable yields. Since it is known that diaryltellurium dihalides are reduced to diaryl tellurides by MeMgI [18], the coupling reaction observed here is essentially the same as that described above and may proceed through di-*p*-methoxyphenyl telluride. In fact, a considerable amount of di-*p*-methoxyphenyl telluride was found in the products. Similar treatment of

TABLE 3

CROSS-COUPLING BETWEEN **5** OR OTHER TELLURIUM COMPOUNDS AND GRIGNARD REAGENTS (RMgBr)[a]

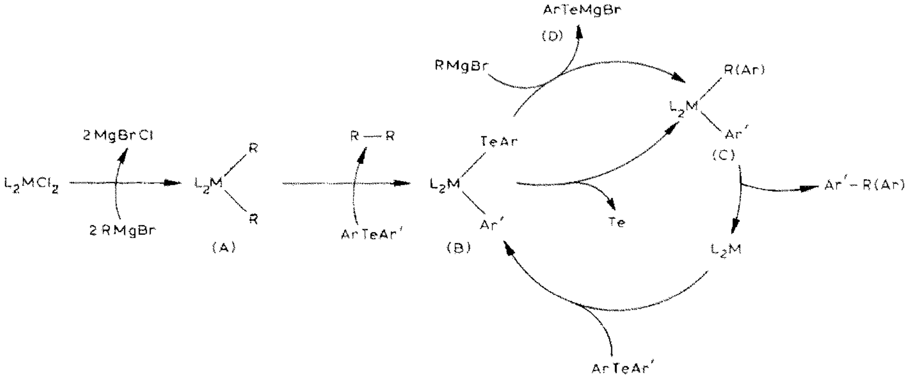
Ar in **5** or other Te compound (1 mmol)	R (2.5 mmol)	Catalyst[b] (0.05 mmol)	Reaction temp. (°C)	Reaction time (h)	Product and yield (mmol)[c]			
					6	**7**	**8**	Ar_2Te[d]
p-$MeOC_6H_4$	Ph	A	15	0.17	0.35	0.30	0.32	–[e]
p-$MeOC_6H_4$	Ph	A	20	5	0.97	0.22	0.54	–[e]
p-$MeOC_6H_4$	Ph	A	67	3	0.95	0.21	0.40	0.31
p-$MeOC_6H_4$	Ph	C	15	0.17	0.40	0.18	0.48	0.62
p-MeC_6H_4	Ph	A	67	3	1.14	0.27	0.37	0.25
Ph	p-$MeOC_6H_4$	A	20	5	0.78	0.18	0.29	–[e]
Ph	p-MeC_6H_4	A	15	0.17	0.73	0.15	0.35	0.26
Ph	Hexyl	A	67	3	0.22	0.17	0.21	0.17
Ph	Hexyl	B	67	3	0.24	0.07	0.19	0.74
Ph	Hexyl	A	15	0.17	0.08	0.15	0.44	0.44
Ph[f]	Hexyl	A	35	8	0.12	0.33	0.83	–[e]
Ph[f]	Hexyl	B	35	8	0.44	0.36	0.24	0.42
PhTe-Hexyl	Hexyl	A	67	3	0.26[g]		0.24[h]	–[e]
PhTe-Hexyl	Hexyl	B	67	3	0.21[g]		0.22[h]	–[e]
PhTe-Hexyl	Ph	A	67	3	0.07[g]		0.58[i]	–[e]
$(p$-$MeOC_6H_4)_2TeCl_2$	Ph	A	15	0.17	0.62	0.33	0.87	0.33
$(p$-$MeOC_6H_4)_2TeCl_2$	Ph	A	67	3	0.42	0.19	0.64	0.45
p-$MeOC_6H_4TeCl_3$	Ph	A	67	3	0.10	trace	0.55	–[e]

[a] Carried out in THF (10 ml) under N_2. [b] See footnote of Table 1. [c] Determined by GLC. [d] Recovered or produced. [e] Not determined. [f] Diethyl ether as solvent. [g] Hexylbenzene. [h] Dodecane. [i] Biphenyl.

p-methoxyphenyltellurium trichloride gave the expected 4-methoxybiphenyl only in low yield.

Considering the proposed mechanism for the Ni^{II}-phosphine complex-catalyzed cross-coupling between organic halides and Grignard reagents [13], a possible mechanism for the coupling of **1** (R = Ph) and **5** with a Grignard reagent shown in Schemes 1 and 3 seems to involve the formation of diorgano-nickel or -cobalt intermediate (A) which is subsequently converted by the organic telluride to an aryltelluro(organo)-nickel or -cobalt complex (B) (Scheme 4). The intermediate B [19] may deposit elemental tellurium to give another diorganometal intermediate (C) directly, and/or it reacts with Grignard reagent to give C together with aryltelluromagnesium bromide (D) [20]. A catalytic cycle involving organonickel-(I) and -(III) species and their cobalt analogues such as L_2MCl and $L_2MCl(Ar)R$ (M = Ni, Co; L = phosphine) is also conceivable as an alternative mechanism as has been proposed by Kochi for Ni^{II}-phosphine-catalyzed coupling of aryl halides [21] and cross-coupling of organic halides with Grignard reagents [22]. At the present time we have no results which would support one or the other.

SCHEME 4



Although it has been reported that Pd^0- and Pd^{II}- complexes are very effective catalysts for stereoselective cross-coupling of alkenyl halides with Grignard reagents [23], these did not work well in the case of alkenyl telluride **1** (R = Ph) as shown in Table 1. A key step of the former reaction is the oxidative addition of alkenyl halide to Pd^0 to produce an alkenylpalladium(II) which begins a catalytic reduction-oxidation cycle [23,24]. On the other hand, in the latter reaction **1** (R = Ph) may work mainly as a ligand for Pd^0 or Pd^{II} to give some complexes as has already been found for many organic tellurides [25]. In the case of Ni or Co, attempts to prepare complexes containing any organic tellurium compound except $(\pi\text{-Cp})(Bu_3P)Ni\text{-}TeAr$ [19] were reported to be unsuccessful [25].

Finally, as to the coupling reaction of **1** (R = CO_2Et) (Scheme 2) we do not have any reasonable explanation yet. The formation of diphenyl telluride in the absence of metal catalyst which has also been observed in the case of **1** (R = Ph) may be due to the direct attack of the phenyl moiety of PhMgBr on tellurium. In the light of the complete inversion at the vinylic carbon bearing the phenyltellurium moiety to give **4**, Ni^{II}- or Co^{II}-phosphine complex-catalyzed 1,4-addition of PhMgBr to the α,β-unsaturated ester might occur instead of the formation of such an intermediate as B in Scheme 4, followed by elimination of phenyltellurolate ion ($PhTe^-$). Such a type of reaction has precedents in the Ni(acac)$_2$-catalyzed 1,4-addition of organoaluminum [26] and organozirconium [27] compounds to α,β-unsaturated ketones.

Experimental

^{1}H NMR spectra were recorded with JEOL JNM FX-100 (100 MHz) and Varian HR-220 (220 MHz) instruments on solutions in $CDCl_3$ with Me_4Si as an internal standard. ^{13}C NMR spectra were taken at 25.1 MHz with a JEOLCO ^{13}C Fourier transform NMR system and were recorded on solutions in $CDCl_3$, after 250–1000 pulses with intervals of 2.7–2.8 s. GLC analyses were carried out using a Shimadzu 4CMPF apparatus using Silicone QF-1(5%)-Chromosorb-W(1 m), PEG 6000 (25%)-Shimalite (1 and 3 m) and EGSS-X (15%)-Chromosorb-W(1 m) columns (N_2 as carrier gas). IR spectra were recorded with a Hitachi EPI-S2 spectrometer. Mass spectra were measured on a JEOL JMS-DX 300 mass spectrometer, equipped with a JMA-3500 data processing system. The ionization voltage was 70 eV for all compounds. Melting points were determined with a Shimadzu MM-2 micro melting point determination apparatus and were uncorrected. Commercially available Te and $TeCl_4$ (Nakarai Chemicals) and magnesium turnings (Wako Pure Chemical) were used without further purification, while commercial organic compounds were distilled immediately before use: i.e., tetrahydrofuran (THF) was distilled from $LiAlH_4$ and diethyl ether was dried over sodium and then distilled. Aryltellurium trichlorides, diaryltellurium dichlorides and diaryl tellurides were prepared as reported previously [2,6]. Hexyl phenyl telluride was prepared from the reaction of hexyl bromide with phenyltellurolate ion [28]. Various phosphine-metal complexes were prepared by known methods or were commercial products; $NiCl_2(PPh_3)_2$ [29], $CoCl_2(PPh_3)_2$ [30], $PdCl_2(PPh_3)_2$ [31], $Pd(PPh_3)_4$ [32] and $PdCl_2(PhCN)_2$(Ventron). $NiCl_2(Ph_2PCH_2CH_2CH_2PPh_2)$ was kindly supplied by Dr. Kohei Tamao of Kyoto University.

Grignard reagents

Grignard reagents were prepared in a standard manner by adding a THF or diethyl ether (20 ml) solution of an organic halide (20 mmol) to magnesium turnings (20 mmol) under N_2. Concentrations of Grignard reagents were determined by a reported method [13]. In a typical run, a freshly prepared THF solution of PhMgBr (2.5 mmol) contains 0.009 mmol of biphenyl and 0.013 mmol of bromobenzene, and after 3 days the solution contains 0.22 mmol of biphenyl. Similarly, a freshly prepared diethyl ether solution of PhMgBr (2.5 mmol) contains 0.14 mmol of biphenyl and 0.20 mmol of bromobenzene. On the other hand, octane was hardly observed in a freshly prepared THF or diethyl ether solution of BuMgBr.

Preparation of vinyl tellurides (1)

To an ethanol solution (10 ml) of diphenyl ditelluride (2.05 g, 5 mmol) [33] was added an ethanol solution (10 ml) of $NaBH_4$ (0.50 g, 13.2 mmol) at room temperature under N_2, during which period the color of the solution turned from orange to pale yellow. Phenylacetylene (1.1 g, 10.8 mmol) was then added to the resulting solution and the mixture was stirred at reflux for 20 h. After cooling, the mixture was treated with aq. NaCl and extracted with $CHCl_3$ (50 ml × 3), and the extract was dried over $MgSO_4$. Evaporation of $CHCl_3$ left a yellow-orange oil which was

subjected to column chromatography (silica gel) [hexane-ethyl acetate (10 : 1) as eluant] to give a yellow solid of **1** (R = Ph) (2.15 g, 7.0 mmol, 70% yield) which was recrystallized from ethanol: m.p. 43–44°C.
(Found: C, 54.62; H, 3.94. $C_{14}H_{12}Te$ calcd.: C, 54.62; H, 3.90%.) ^1H NMR (220 MHz, $CDCl_3$); δ(ppm) 7.07 (d, 1H, J = 11 Hz), 7.15–7.35 (m, 8H), 7.45 (d, 1H, J = 11 Hz), 7.73 (d, 2H, J = 7 Hz). IR; 3060, 3030, 1600, 1570, 1485, 1470, 1440, 1430, 1325, 1310, 1180, 1145, 1080, 1065, 1015, 995, 910, 820, 770s, 735s, 705s, 695s, 680s, 660 cm^{-1}. Mass spectrum, m/e (relative intensity, only peaks stronger than 10% of the base peak above m/e 50) 310 (M^+, 20.9), 308 (M^+, 19.4), 306 (M^+, 12.3), 181(13), 180(94), 179(66), 178(13), 155(24), 103(55), 102(28), 78(29), 77(100), 76(12), 51(49), 50(15). ^{13}C NMR ($CDCl_3$); δ(ppm) 109.0 (d, PhTeC=), 115.2 (s, PhTe, C(1)), 126.0 (d, Ph, C(4)), 127.3 (d, Ph, C(2)), 128.0 (d, PhTe, C(4)), 128.4 (d, Ph, C(3)), 129.3 (d, PhTe, C(3)), 136.8 (d, =CPh), 137.8 (d, PhTe, C(2)), 138.8 (s, Ph, C(1)).

Similar treatment of ethyl propiolate and propargyl alcohol afforded **1** (R = CO_2Et) and **1** (R = CH_2OH) in a yield of 100% and 92%, respectively, as an orange oil, the latter being slightly unstable. Some physical data are as follows: **1** (R = CO_2Et) (Found: C, 43.94; H, 4.06. $C_{11}H_{12}O_2Te$ calcd.: C, 43.49; H, 3.98%.) ^1H NMR (100 MHz, $CDCl_3$); δ(ppm) 1.32 (t, 3H), 4.28 (q, 2H), 6.96 (d, 1H, J = 10 Hz), 7.08–7.48 (m, 3H), 7.60–8.0 (m, 2H), 8.48 (d, 1H, J = 10 Hz). IR; 3180, 3000, 1711, 1677s, 1555s, 1475, 1441, 1369, 1330s, 1210s, 1135, 1029, 804, 731, 692 cm^{-1}. Mass spectrum, m/e (relative intensity, only peaks stronger than 10% of the base peak above m/e 50) 306 (M^+, 27.0), 304 (M^+, 24.7), 302 (M^+, 15.9), 229(17), 227(17.5), 207(13), 205(13), 201(25), 199(20), 197(12), 154(22), 131(54), 103(19), 78(24), 77(100), 51(49), 50(14). ^{13}C NMR ($CDCl_3$); δ(ppm) 14.3(q), 60.9(t), 119.7 (s, Ph, C(1), 122.5 (d, PhTeC=), 128.1 (d, Ph, C(4)), 129.2 (d, Ph, C(3)), 138.0 (d, Ph, C(2)), 140.4 (d, =$C$$CO_2Et$), 168.8(s). **1** (R = CH_2OH) (Found: C, 41.53; H, 4.00. $C_9H_{10}OTe$ calcd: C, 41.29; H, 3.85%.) ^1H NMR (100 MHz, $CDCl_3$); δ(ppm) 2.52 (br, 1H), 4.21 (d, 2H, J = 5 Hz), 6.53 (dt, 1H, J = 10, 5Hz), 6.93 (dt, 1H, J = 10, 1.5 Hz), 7.04–7.32 (m, 3H), 7.56–7.80 (m, 2H). IR; 3400s, 3060, 2920, 2860, 1595, 1570, 1470, 1430, 1300, 1165, 1100, 1040s, 1020, 996, 730s, 690s cm^{-1}.

The addition of phenyltellurol to several other acetylenes has been reported [34].

Coupling reactions

Typical experimental procedures are given below for the reaction of **1** (R = Ph) with PhMgBr in THF.

To a THF solution (10 ml) of **1** (R = Ph) (0.307 g, 1.0 mmol) containing $NiCl_2(PPh_3)_2$ (0.032 g, 0.05 mmol) was added a THF solution (1 M) of PhMgBr (2.5 ml, 2.5 mmol) under N_2 at 20°C. The mixture was stirred for 10 min during which period a black precipitate of elemental tellurium was formed. The mixture was then decomposed with dil. HCl and filtered from the precipitates which were washed to leave black tellurium (0.11 g). The filtrate was treated with aq. NaCl and extracted with diethyl ether (3 × 30 ml) and the extract was dried over $MgSO_4$. GLC analysis of the extract revealed the presence of biphenyl (0.142 g, 0.92 mmol) and *cis* and *trans*-stilbene (0.108 g, 0.60 mmol; *cis/trans* = 90/10), dibenzyl being used as an internal standard.

Authentic samples for β-butylstyrenes [*Z*- and *E*-**2** (R′ = Bu)] were prepared by the reported method [13] from a mixture of *cis*- and *trans*-β-bromostyrenes and butylmagnesium bromide in THF in the presence of $NiCl_2(PPh_3)_2$: yield 60%, *m/e* 160. IR and NMR data are identical with the reported ones [24].

Commercially available *cis*- and *trans*-stilbenes, ethyl cinnamate, biphenyl, 4-methylbiphenyl, 4-methoxybiphenyl, 4,4'-dimethoxybiphenyl, butylbenzene, hexylbenzene, octane, and dodecane were used as authentic samples for GLC analyses.

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