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Stereoselective Synthesis of Enynes by Nickel-Catalyzed Cross-Coupling of Divinylic Chalcogenides with Alkynes

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Abstract: (*Z*,*Z*)- and (*E*,*E*)-divinylic selenides and telurides undergo direct coupling with terminal alkynes in the presence of a nickel/CuI catalyst at room temperature to give (*Z*)- and (*E*)-enyne systems in good yields and with complete retention of configuration.

Conjugated enynes are of great interest in organic synthesis. Calicheamicins, esperamicins, and dynemycins are members of a newly emerged class of antibiotic molecules that was discovered recently. They are considered to be some of the most potent antitumoral agents known to date and have other interesting biological activities as well.[1,2] The synthesis of enynes has received special attention during the last 20 years, and new methods for their preparation from vinyl halides or vinyl organometallic compounds have been recently developed. The cross-coupling of vinyl bromides, iodides, chlorides, and triflates with monosubstituted acetylenes has been achieved in the presence of a Pd^0 or Pd^{II}/CuI catalyst using an amine as a base.[3] The synthesis of enynes has also been performed using the coupling reaction of bromoalkynes with vinylmetals such as vinyl boron,[4] -copper,[5] -zinc,[6] -aluminum,[7] or -magnesium reagents[8] by the copper-catalyzed coupling reaction of alkynes with alkenyliodonium salts[9] and vinyl iodides[10] and by the coupling of 1-silylacetylenes with vinyl halides and triflates.[11] The use of vinylic chalcogenides to obtain enyne and enediyne systems has been previously described,[12] and many other important applications of vinylic selenides and vinylic tellurides have also been reported.[13] However, just a few of them involved (*Z*,*Z*)-divinylic tellurides, while similar applications of (*E*,*E*)-divinylic tellurides and selenides are virtually unknown. In this way, (*Z*,*Z*)-divinylic tellurides undergo, in a stereoselective manner, transmetalation reactions to give vinyllithium[14] and vinylcopper[12a,d,15] species, useful intermediates for further reactions with electrophiles. They have also been converted to the corresponding coupling products by reaction with lower order cyanocuprates[16] and to cross-coupling[17] and homocoupling products (1,4-diaryl-1,3-butadienes) by treatment with palladium catalysts.[18]

Recently, we accomplished the stereospecific formation of (*Z*)-enyne systems by the palladium-catalyzed cross-coupling reaction of (*Z*,*Z*)-divinyl tellurides with 1-alkynes.[19] Although, in all cases, an excess of alkyne has been used, the transfer of only one vinylic group was observed. Divinylic selenides were totally inert under these coupling conditions, employing several different palladium catalysts, and the starting materials have usually been recovered unchanged. Herein we report a more general approach of this method for the direct synthesis of (*Z*)- and (*E*)-enyne systems via a nickel-catalyzed cross-coupling reaction of (*Z*,*Z*)- and (*E*,*E*)-divinylic chalcogenides with 1-alkynes. In this method,

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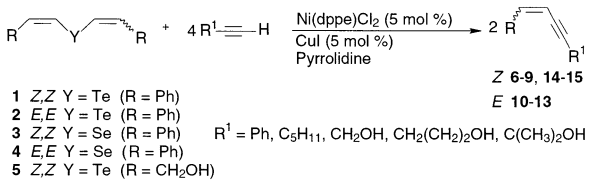
SCHEME 1



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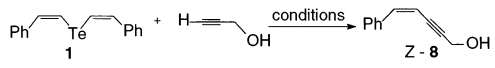


the transfer of both vinylic groups linked to the chalcogen atom was observed, as summarized in Scheme 1.

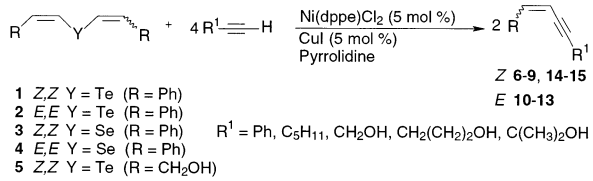
The initial studies were focused on the development of an optimum set of reaction conditions for the coupling reaction of divinylic chalcogenides with terminal alkynes. In preliminary experiments, we investigated the catalyzed cross-coupling between (*Z*,*Z*)-distyryl telluride **1** (1 equiv) and 2-propyn-1-ol (4 equiv) in pyrrolidine, at room temperature (Scheme 2).

The influence of the nature of the catalyst is noteworthy. When the reaction was performed in pyrrolidine using $PdCl_2(PhCN)_2$, $Pd(OAc)_2$, $PdCl_2$, $PdCl_2/PPh_3$, $PdCl_2(PPh_3)_2$, $Pd(PPh_3)_4$, or $Pd(PPh_3)_4$/CuI, no coupling product was isolated. The change of the catalyst to $Ni(PPh_3)_2Cl_2$ gave the desired enynes in unsatisfactory yields (20−40%), depending on the amount of catalyst used (1−5 mol %). However, using Ni(dppe)Cl_2 (5 mol %), in the presence of a copper salt (CuI, 5 mol %), afforded enyne (*Z*)-**5** in 77% isolated yield. Lower yields were obtained in the presence of other solvents or mixtures of solvents such as THF, DMF, CH_3CN, CH_2Cl_2, THF/methanol, benzene, and DMF/methanol. Thus, the optimum conditions for coupling according to Scheme 1 were stablished to be the use of Ni(dppe)Cl_2 (5 mol %), CuI (5 mol %), pyrrolidine (10 mL), divinyl chalcogenide (1 mmol), and the appropriate 1-alkyne (4 mmol) at room temperature. Moreover, the coupling reaction was then extended to other divinylic chalcogenides **2**−**4** and alkynes. Fortunately, this condition proved to be efficient for the (*E*,*E*)-isomers of selenium and tellurium derivatives and also for the (*Z*,*Z*)-divinyl selenide. The results are summarized in Table 1.

The reaction was equally successful with the divinylic telluride **5**, a substrate containing free OH groups. The cross-coupling reaction of **5** with 1-heptyne and 2-methyl-3-butyn-2-ol gave the corresponding enynes **14** and **15** in good yields (entries 17 and 18, Table 1).

Noteworthy is the efficiency of this coupling reaction using a nickel catalyst. To our knowledge, this reaction is one of the first examples of an efficient cross-coupling reaction involving a terminal alkyne catalyzed by nickel, since in almost all examples described to date, only palladium catalysts have been used with efficiency.[3h,20] Also, all described examples of efficient cross-coupling involving vinylic tellurides have utilized palladium catalysts (in up to 20 mol % of catalyst), while alkyl or aryl Grignard reagents have been shown to couple with vinylic

TABLE 1. Synthesis of Enynes by Cross-Coupling Reaction of Divinylic Chalcogenides with 1-Alkynes



	substrate	alkyne R^1	enyne	time (h)	yield[a] (%)
1	(*Z*,*Z*)-1	*n*-pentyl	6	20	78
2	(*Z*,*Z*)-1	Ph	7	16	61
3	(*Z*,*Z*)-1	CH_2OH	8	20	73
4	(*Z*,*Z*)-1	$CH_2CH_2CH_2OH$	9	20	72
5	(*E*,*E*)-2	*n*-pentyl	10	20	57
6	(*E*,*E*)-2	Ph	11	16	72
7	(*E*,*E*)-2	CH_2OH	12	15	81
8	(*E*,*E*)-2	$CH_2CH_2CH_2OH$	13	20	68
9	(*Z*,*Z*)-3	*n*-pentyl	6	20	61
10	(*Z*,*Z*)-3	Ph	7	20	54
11	(*Z*,*Z*)-3	CH_2OH	8	16	56
12	(*Z*,*Z*)-3	$CH_2CH_2CH_2OH$	9	22	76
13	(*E*,*E*)-4	*n*-pentyl	10	22	71
14	(*E*,*E*)-4	Ph	11	20	63
15	(*E*,*E*)-4	CH_2OH	12	20	75
16	(*E*,*E*)-4	$CH_2CH_2CH_2OH$	13	20	83
17	(*Z*,*Z*)-5	*n*-pentyl	14	20	71
18	(*Z*,*Z*)-5	$C(CH_3)_2OH$	15	24	61

[a] Yield of isolated pure product.

selenides in the presence of nickel catalysts.[21] The advantages of the nickel system include its air stability, lower cost, and ease of preparation of the catalyst, all of which are important when considering the scale-up of a reaction.

Analysis of the ^1H NMR and ^{13}C NMR spectra showed that all the enyne compounds presented data in full agreement with their assigned structures. The stereochemistry of the obtained enynes was easily established. As an example, the ^1H NMR spectrum of compound **6** showed a double triplet at 5.69 ppm with coupling constants of 11.8 and 2.4 Hz, typical of a cis hydrogen. The other vinylic hydrogen resonates at 6.54 ppm as a doublet, with a coupling constant of 11.8 Hz. The stereoisomeric purities of enynes **6**−**9** were similar to that of starting divinylic telluride **1**, due to a complete retention of configuration in this type of reaction. If the reactions were performed with pure (*E*,*E*)- or (*Z*,*Z*)-isomers, pure (*E*)- or (*Z*)-enynes were isolated in all cases. By using an enriched mixture such as 95:5 , the same ratio was observed in the final product. The only exception was observed with the coupling of (*Z*,*Z*)-isomers **1** and **3** with phenylacetylene. Under the experimental conditions employed, isomerization of enyne **7** occurred, and the same 93:7 mixture of (*Z*/*E*)-isomers was isolated, starting with either telluride **1** or selenide **3**.

The starting divinylic chalcogenides have been prepared by procedures previously described or by methods under study in our laboratory. In this way, (*Z*,*Z*)-divinylic

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telluride **1** was prepared by the reaction of phenyl acetylene with a solution of sodium telluride, generated in situ, in 79% isolated yield.[12a,15b] The (*E*,*E*)-isomers were prepared by Na_2Y (Y = Se, Te) vinylic substitution of (*E*)-*β*-bromostyrene (70 and 82% yields, respectively).[22] Using a commercially available (~9:1) *E*/*Z* mixture of isomers of bromostyrene allowed the pure (*E*,*E*)-isomer to be isolated after column chromatography and washing with petroleum ether or by starting with the pure (*E*)-*β*-bromostyrene, easily available by recently described procedures.[23] (*Z*,*Z*)- and (*E*,*E*)-divinylic selenides are also available by a procedure published some years ago, involving the reaction of (*Z*)- and (*E*)-*β*-styryl selenide anions, generated in situ, with (*Z*)- and (*E*)-*β*-bromostyrene, respectively.[24] Otherwise, we prefer to prepare these species by a method under investigation in our laboratory. (*Z*,*Z*)-Divinylic selenide **3** was obtained by the reaction of phenylacetylene with Na_2Se, in 71% isolated yield, in a procedure similar to the one used for the preparation of the divinyl tellurium derivative (*E*,*E*)-**2**.[12a,15b] We observed that the use of 1-propanol instead of ethanol in this reaction was necessary and allows for easy entry to this class of compounds.[25]

In summary, we have explored a new Ni/CuI-catalyzed cross-coupling reaction of the (*Z*,*Z*)- and (*E*,*E*)-divinylic chalcogenides with alkynes and established a new stereoselective route to (*Z*)- and (*E*)-enynes in good yields. Our approach is an improvement of the described methods, since it avoids the preparation of vinylmetals and haloalkynes and requires no protection of the hydroxyl group in propargylic alcohol. In comparison to our previously described method, the present procedure has advantages such as the easy access and the great stability of the divinylic chalcogenides and the transfer of both of the vinylic units.

Experimental Section

General Methods. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 200 or 50 MHz, respectively. Melting points are uncorrected. HRMS were obtained at Central Analítica, Instituto de Química, UNICAMP, or Universidade de São Paulo, SP, Brazil. All reagents and solvents were dried and purified before use by the usual procedures prior to use. Column chromatography was carried out on 230−400 mesh silica gel.

(*Z*)-1-(1-Nonen)-3-ynylbenzene (6). Typical Procedure for the Coupling of (*Z*,*Z*)-Bis-styryltelluride ((*Z*)-1) with 1-Alkyne. To a two-necked 25 mL round-bottomed flask under an argon atmosphere containing $Ni(dppe)Cl_2$ (0.026 g, 5 mol %), CuI (0.01 g, 5 mol %), and dry pyrrolidine (1.5 mL) was added (*Z*,*Z*)-**1** (0.33 g, 1.0 mmol). After the mixture was stirred for 15 min at room temperature, 1-heptyne (0.38 g, 4.0 mmol) was added. An exothermic reaction was observed, and the temperature was maintained between 15 and 20 °C by using a water bath. The reaction was stirred at room temperature for 20 h. The solids were filtered off over Celite; the filtrate was treated with a saturated solution of NH_4Cl and extracted with ethyl acetate, and the organic layers were dried over $MgSO_4$ and concentrated in vacuo. Column chromatography (hexanes) of the residue gave (*Z*)-**6** as a pale yellow oil (0.308 g, 78%): IR (neat, cm^{-1}) 3061, 3021, 2200, 1660, 1450, 784, 692; ^{1}H NMR ($CDCl_3$) *δ* 7.85 (d, *J* = 6.8 Hz, 2H), 7.37−7.20 (m, 3H), 6.54 (d, *J* = 11.8 Hz, 1H), 5.69 (dt, *J* = 11.8, 2.4 Hz, 1H), 2.43 (td, *J* = 8.0, 2.0 Hz, 2H), 1.63−1.33 (m, 6H), 0.91 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$) *δ* 137.18, 136.70, 128.41, 128.10, 128.07, 108.20, 97.80, 79.20, 31.14, 28.27, 22.21, 19.84, 13.94; EIMS *m*/*z* (rel int) 198 (25), 155 (20), 141 (100), 91 (27), 79 (12); HRMS calcd for $C_{15}H_{18}$ 198.1408, found 198.1417.

(*Z*)-1,4-Diphenyl-1-buten-3-yne (7):[26] oil; IR (neat, cm^{-1}) 3060, 3022, 2184, 1594, 1448, 1441; ^{1}H NMR ($CDCl_3$) *δ* 7.90 (d, *J* = 8.0 Hz, 2H); 7.49−7.22 (m, 8H), 6.65 (d, *J* = 12.0 Hz, 1H), 5.89 (d, *J* = 12.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) *δ* 138.64, 136.5, 131.42, 128.73, 128.48, 128.38, 128.34, 128.26, 123.42,107.35, 95.83, 88.22; EIMS *m*/*z* (rel int) 204 (base), 203 (95), 202 (97), 101 (50), 89 (16), 76 (15), 63 (7), 51 (7).

(*Z*)-5-Phenyl-4-penten-2-yn-1-ol (8): oil; IR (neat, cm^{-1}) 3329, 3023, 2860, 1951, 1899, 1598, 1492; ^{1}H NMR ($CDCl_3$) *δ* 7.81 (d, *J* = 8.0 Hz, 2H), 7.39−7.23 (m, 3H), 6.64 (d, *J* = 12.0 Hz, 1H), 5.71 (dt, *J* = 12.0, 2.0 Hz, 1H), 4.46 (s, 2H), 2.27 (s, 1H); ^{13}C NMR ($CDCl_3$) *δ* 139.10, 136.14, 128.53, 128.51, 128.36, 106.68, 93.80, 83.98, 51.65; EIMS *m*/*z* (rel int) 158 (53), 140 (41), 129 (95), 128 (100), 127 (40), 115 (38), 102 (11), 77 (18), 63 (23), 51 (27); HRMS calcd for $C_{11}H_{10}O$ 158.0731, found 158.0737.

(*Z*)-7-Phenyl-6-hepten-4-yn-1-ol (9):[27] oil; ^{1}H NMR ($CDCl_3$) *δ* 7.83 (d, *J* = 8.2 Hz, 2H), 7.37−7.21 (m, 3H), 6.54 (d, *J* = 11.8 Hz, 1H), 5.67 (dt, *J* = 11.8, 2.4 Hz, 1H), 3.73 (t, *J* = 6.2 Hz, 2H), 2.53 (td, *J* = 6.9, 2.4 Hz, 2H), 2.05 (s, 1H), 1.81 (quint., *J* = 6.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) *δ* 137.51, 136.50, 129.47, 128.64, 128.31, 107.85, 96.53, 79.49, 61.42, 31.14, 16.51; EIMS *m*/*z* (rel int) 186 (52), 167 (27), 155 (28), 153 (56), 141 (85), 129 (50), 128 (48), 115 (100), 91 (35), 77 (20), 63 (23), 51 (22); HRMS calcd for $C_{13}H_{14}O$ 186.1044, found 186.1051.

(*E*)-1-Phenyl-1-nonen-3-yne (10):[10b] oil; IR (neat, cm^{-1}) 2956, 2932, 2859, 2210, 1704, 1596, 1449;^{1}H NMR ($CDCl_3$) *δ* 7.35−7.21 (m, 5H), 6.85 (d, *J* = 16.0 Hz, 1H), 6.14 (dt, *J* = 16.0, 2.1 Hz, 1H), 2.34 (td, *J* = 6.0, 2.0 Hz, 2H), 1.59−1.35 (m, 6H), 0.91 (t, *J* = 7.1 Hz, 3H), ^{13}C NMR ($CDCl_3$) *δ* 139.88, 136.60, 128.57, 128.11, 125.98, 108.93, 92.99, 79.72, 31.11, 28.49, 22.20, 19.59, 13.93; EIMS *m*/*z* (rel int) 198 (36), 169 (11), 155 (23), 141 (100), 115 (61), 91 (36), 79 (14).

(*E*)-1,4-Diphenyl-1-buten-3-yne (11): mp 97−98°C (lit.[12h] 96−97 °C).

(*E*)-5-Phenyl-4-penten-2-yn-1-ol (12):[10b] oil; IR (neat, cm^{-1}) 3369, 3027, 2923, 2208, 1732, 1689, 1597, 1492, 1448; ^{1}H NMR ($CDCl_3$) *δ* 7.36−7.21 (m, 5H), 6.95 (d, *J* = 16.0 Hz, 1H), 6.16 (dt, *J* = 16.0, 4.0 Hz, 1H), 4.43 (d, *J* = 2.0 Hz, 2H), 2.06 (s, 1H); ^{13}C NMR ($CDCl_3$) *δ* 141.81, 135.95, 128.62, 128.54, 126.23, 107.37, 89.40, 84.80, 51.52; EIMS *m*/*z* (rel int) 158 (52), 140 (37), 128 (100), 127 (40), 115 (43), 102 (12), 77 (20), 63 (20), 51 (29).

(*E*)-7-Phenyl-6-hepten-4-yn-1-ol (13):[28] oil; IR (neat, cm^{-1}) 3343, 3026, 2946, 2211, 1598, 1491, 1446; ^{1}H NMR ($CDCl_3$) *δ* 7.32−7.20 (m, 5H), 6.86 (d, *J* = 16.0 Hz, 1H), 6.12 (dt, *J* = 16.0, 4.0 Hz, 1H), 3.76 (t, *J* = 6.0 Hz, 2H), 2.48 (td, *J* = 8.0, 4.0 Hz, 2H), 2.09 (s, 1H), 1.80 (quint., *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) *δ* 140.22, 136.34, 128.54, 128.19, 125.96, 108.49, 91.81, 80.19, 61.50, 31.30, 14.86; EIMS *m*/*z* (rel int) 186 (65), 167 (29), 155 (30), 153 (57), 142 (98), 141 (89), 130 (34), 129 (51), 128 (49), 115 (base), 91 (40), 77 (20), 63 (21), 51 (20); HRMS calcd for $C_{13}H_{14}O$ 186.1044, found 186.1019.

(*Z*)-Dec-2-en-4-yn-1-ol (14): oil; spectroscopic data were in good agreement with the literature.[3f]

(2*Z*)-6-Methylhept-2-en-4-yne-1,6-diol (15): oil; IR (neat, cm^{-1}) 3351, 2918, 2851, 1736, 1455, 1369, 1240, 1159, 1026, 940; ^{1}H NMR ($CDCl_3$) *δ* 6.07 (dt, *J* = 10.8, 6.3 Hz, 1H), 5.60 (d, *J* = 10.8 Hz, 1H), 4.38 (dd, *J* = 6.5, 1.2 Hz, 2H), 2.12 (s, 2H), 1.54 (s, 6H); ^{13}C NMR ($CDCl_3$) *δ* 141.4, 110.1, 100.0, 73.3, 65.2, 60.4, 31.2; HRMS calcd for $C_8H_{12}O_2$ 140.0837, found 140.0834.

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Supporting Information Available: Analytical data for compounds **11** and **14** and ^{1}H and ^{13}C NMR spectra of compounds **6**−**15**. This material is available free of charge via the Internet at http://pubs.acs.org.

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