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Synthesis of symmetrical 1,3-diynes via homocoupling reaction of *n*-butyl alkynyltellurides

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ABSTRACT

An ultrasound-assisted synthesis of symmetrical 1,3-diyne compounds with electron-withdrawing or -donating substituents is described and illustrated by the palladium-catalyzed homocoupling reaction of *n*-butyl alkynyltellurides. This procedure offers easy access to 1,3-diynes in very short reaction times, and the products are achieved in good to excellent yields.

Symmetrical and unsymmetrical alkynes play an important role as building blocks in many synthetic transformations, and in new materials such as conjugated oligomers and polymers, liquid crystals, non-linear materials, molecular wires, and in other engineering materials.[1] Several symmetrical 1,3-diynes have been exclusively used as equivalents to other functional groups in synthetic organic chemistry.[2] In addition, these 1,3-diynes are common structural motifs found in various natural products[3] and important biological activities, specially antifungal activity.[4] In the past two decades, 1,3-diynes have been recognized as an important functionality in organic molecular materials such as molecular wires and molecular architecture on the nanometer scale.[5] Therefore, the need for efficient and concise syntheses of diynes having desired functionalities is evident in natural product chemistry as well as in the discovery of new pharmaceutical agents.

Carbon–carbon bond formation for the preparation of symmetrical and unsymmetrical diyne compounds is one of the most useful and important tools in modern organic chemistry. The construction of diynes can be achieved either by intermolecular- or by intramolecular cross-coupling of two similar or dissimilar alkynylic functionalities in the presence of organo-metal complexes. Palladium-catalyzed cross-coupling reactions between the electrophilic compounds Ar–X (X being mainly Cl, Br, I and OTf) and organometallic species Ar–M (M being Mg, Zn, Sn, and B) are on the verge of truly becoming a general process for the construction of diyne systems.

Numerous synthetic approaches are available for the synthesis of symmetrical 1,3-diynes in the literature, which include the traditional oxidative homocoupling of terminal acetylenes such as Cadiot–Chodkiewicz,[6] Eglington,[7] Glaser,[8] Hay,[2b] Sonogashira couplings[9] and the Pd(0)–Cu(I) catalyzed self-coupling of terminal alkynes in the presence of chloroacetone,[10] iodine,[11] allyl bromide,[12] and ethyl bromoacetate.[13] Recently, Cahiez[14] and others[15] demonstrated the efficiency of the iron-catalyzed homocoupling of alkynyl Grignard reagents using 1,2-dihalogenoethanes as oxidants. Following this, Knochel[16] described the elegant transition-metal-free homocoupling reaction of organomagnesium compounds by direct oxidation with 3,3′,5,5′-tetra-*tert*-butyl-4,4′-diphenoquinone. However, for industrial applications, these methods are limited since they require a stoichiometric amount of organic oxidant.[17] Recently, we reported the synthesis of 1,3-diyne systems by the Cu-mediated homocoupling of potassium alkynylic trifluoroborate salts.[18]

In the current decade, organotellurium compounds have attained remarkable development as synthons and intermediates in synthetic organic chemistry. Organotellurium compounds have been used instead of halogens as electrophilic partners in some palladium-catalyzed cross-coupling reactions.[19,20] Uemura and his research group[21] demonstrated the palladium-catalyzed homocoupling of some organotellurides, such as alkenyl and aryl tellurides, but this approach was associated with poor yields and the formation of some undesired side products. It was also disclosed that homocoupling hardly occurred with tellurides such as diaryl, alkyl aryl, dialkyl and alkynyl aryl tellurides, even in the presence of a stoichiometric amount of palladium salts and at higher temperature.[21a] Barton and his research group[22] also reported the

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homocoupling of some organotellurides but the experimental details are not available.

Recently, we have achieved the palladium-catalyzed homocoupling of *n*-butyl aryltellurides successfully in minutes by using ultrasonic waves as a source of energy.[23] The ultrasound effects are attributed to a physical process called cavitation.[24]

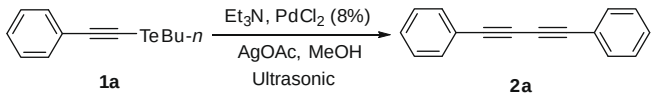
Herein, we report a new protocol for the synthesis of 1,3-diyne systems by the palladium-catalyzed homocoupling of functionalized *n*-butyl alkynyltellurides using ultrasonic waves as a source of energy. The strength of the procedure lies in formation of the C–C bond and in the introduction of electron-donor or -acceptor functionalities into the molecule.

The approach to prepare 1,3-diyne compounds **2a–j** was based on the palladium-catalyzed homocoupling reaction of functionalized *n*-butyl alkynyltellurides **1a–j**. The parent precursors *n*-butyl alkynyltellurides **2a–j** were conveniently prepared in high yields by the lithiation of terminal alkynes followed by the addition of metallic tellurium and *n*-bromobutane.[25]

Initially, we paid attention to the determination of the optimal conditions for the homocoupling of alkynyltelluride **1**. Toward this end, *n*-butyl phenylacetylenic telluride **1a** was chosen as a model substrate and a variety of conditions were screened (Table 1). The reactions were monitored by TLC or GC.

In order to find an appropriate catalyst for the homocoupling of *n*-butyl phenylacetylenic telluride **1a**, we tested several reactions with palladium and non-palladium catalysts. The reactions with the palladium catalysts were successful in most cases. The Pd(II) and (0) species were used in these homocoupling reactions and the best result was obtained with $PdCl_2$ (Table 1, entry 2).

Table 1
Study of the effect of a catalyst on the homocoupling of *n*-butyl phenylacetylenic telluride **1a**



1a **2a**

Entry	Catalyst[a]	Yield[b] (%)
1	—	nr
2	$PdCl_2$	95
3	$PdCl_2(BzCN)_2$	88
4	$Pd(PPh_3)_4$	91
5	CuI	nr
6	$PdCl_2(dppf)CH_2Cl_2$	71
7	$Fe(Acac)_3$	60
8	$Pd(OAc)_2$	92

[a] 10 mol % of catalyst was used.
[b] The yield was determined by GC analysis.

Table 2
Study of the effects of additive and base on the homocoupling of *n*-butyl phenylacetylenic telluride **1a**

Entry	Base	Additive (equiv)	$Pd(PPh_3)_4$ (mol %)	Yield[a] (%)
1	Et_3N	—	$PdCl_2$ (10)	nr
2	Et_3N	AgOAc (1)	$PdCl_2$ (10)	98
3	Et_3N	Ag_2O (1)	$PdCl_2$ (10)	31
4	Et_3N	CuI (1)	$PdCl_2$ (10)	67
5	Et_3N	AgOAc (2)	$PdCl_2$ (10)	81
6	—	AgOAc (1)	$PdCl_2$ (10)	nr[a]
7	Na_2CO_3	AgOAc (1)	$PdCl_2$ (10)	92
8	DIPEA	AgOAc (1)	$PdCl_2$ (10)	95
9	Et_3N	AgOAc (1)	$PdCl_2$ (5)	71
10	Et_3N	AgOAc (1)	$PdCl_2$ (8)	98

[a] The yield was determined by GC analysis.

AgOAc was used as an additive, triethylamine used as the base, and methanol used as the solvent. The reaction was irradiated for 20 min in an ultrasound bath. The product was obtained in 95% yield.

The next step was the determination of the best base and the necessity of an additive in the reaction. Initially, organic bases such as triethylamine and diisopropyl ethyl amine (DIPEA) were used in the presence of AgOAc and the desired compound was observed in 98 and 95% yields respectively (Table 2, entries 2 and 8). When the same reaction was performed with an inorganic base, such as sodium carbonate, the desired compound was achieved in 92% yield (Table 2, entry 7). In order to verify the effect of the base we performed the same reaction without base, but no reaction was observed (Table 2, entry 6).

In order to investigate the effect of the additive, the same reaction was performed with three different additives, mainly AgOAc, Ag_2O, and CuI, and the desired product **2a** was achieved in 98, 31 and 67% yields, respectively (Table 2, entries 2–4). To establish the stoichiometry of the reaction, we performed this reaction with two equivalents of Ag_2OAc, and the desired compound was achieved in 81% yield (Table 2, entry 5). No reaction was observed in the absence of additive (Table 2, entry 1).

In order to achieve the best solvent, we performed different reactions with different kinds of solvents. The best result was achieved with a polar protic solvent (methanol) in 98% yield (Table 3, entry 1). The optimizations results with different solvents are described in Table 3.

During the optimization studies for 1,4-diphenylbuta-1,3-diyne **2a**, it was observed that the reaction mixture containing 1.0 equiv of *n*-butyl phenylacetylenic telluride **1a**, 1.0 equiv of Ag_2OAc, 2.0 equiv of triethylamine, and 8 mol % of $PdCl_2$ in methanol, irradiated under ultrasonic waves for 15 min, was the best for the synthesis of 1,4-diphenylbuta-1,3-diyne **2a**. After achieving the best conditions for the synthesis of the desired compound **2a**, we synthesized a series of symmetrical 1,3-diyne compounds **2a–j** using the optimized conditions in 77–91% yields (see Table 4). Interestingly this reaction worked nicely with both aliphatic and aromatic acetylenic tellurides. All synthesized compounds were characterized by spectroscopic analysis.[32]

On the basis of available literature[21a] we propose a possible catalytic cycle for the homocoupling reaction of *n*-butyl alkynyltellurides as described in Figure 1. According to this cycle, the reaction proceeds with the formation of a telluride-palladium(II) complex (**A**) followed by the transmetallation of the alkynyl group to give the alkynyl palladium species (**B**), which reacts with another alkynyltelluride molecule to give a dialkynyl palladium intermediate (**C**). On reductive elimination the intermediate C undergo homocoupling to give product **2** and Pd. The palladium species is later oxidized with AgOAc to give palladium(II) thus completing the cycle. We observed the formation of dibutyltelluride in trace amounts by GC–MS.

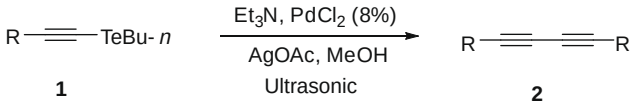
In summary, we have demonstrated the ultrasound-assisted synthesis of alkyl and aryl substituted 1,3-diynes by the homocoupling reaction of easily accessible alkynyltellurides. This methodology has the flexibility of introducing electron-donor or -acceptor

Table 3
Study of the solvent effect on the homocoupling of *n*-butyl phenylacetylenic telluride **1a**

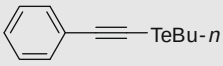
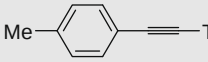
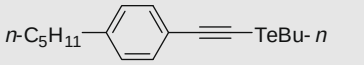
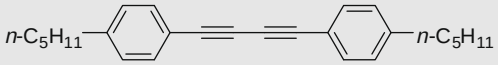
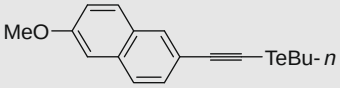
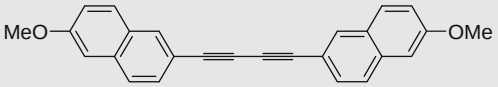
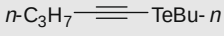
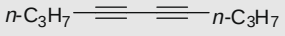
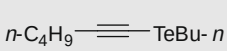
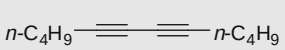
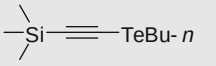
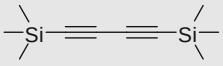
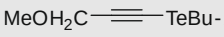
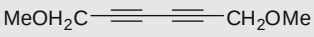
Entry	Solvent	Yield[a] (%)
1	MeOH	98
2	MeCN	21
3	THF	10
4	Dioxane	19

[a] The yield was determined by GC analysis.

Table 4
Homocoupling reaction of functionalized *n*-butyl alkynyltellurides **1a–j**



1 2

Entry	Alkynyltellurides	Products	Reaction time (min)	Yields[a] (%)
a			15	85
b			20	87
c			15	85
d			20	91
e			20	82
f			20	87
g			15	75
h			20	80
i			20	77
j			20	85

[a] Isolated yields.

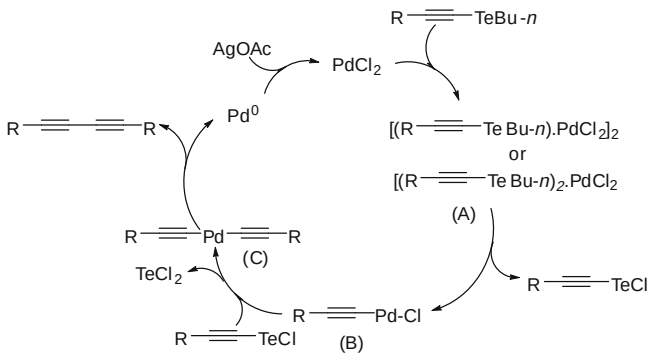


Figure 1. Possible catalytic cycle of the homocoupling reaction of *n*-butyl alkynyltellurides.

functionalities in the 1,3-diynes. Further applications of our methodology for the synthesis of substituted diynes are currently in progress.

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32. *General experimental procedure for 1,3-diyne compounds* **2a–j**: A suspension of alkynyl telluride (**1a**) (0.1435 g, 0.5 mmol), $PdCl_2$ (0.08 g, 8 mmol %), triethylamine (0.101 g, 1 mmol), and silver(I) acetate (0.083 g, 0.5 mmol) in 5 mL of methanol was irradiated in a water bath of an ultrasonic cleaner for 15 min. Then, the reaction was diluted with ethyl acetate (25 mL). The organic layer was washed with a saturated solution of NH_4Cl (2×10 mL) and water (2×10 mL), dried over $MgSO_4$, and concentrated under vacuum. The crude product was purified by flash silica column chromatography using hexane as the eluent and characterized as 1,4-diphenylbuta-1,3-diyne **2a**:[26] white solid; mp 86–88 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30–7.38 (m, 6H, ArH), 7.47–7.56 (m, 4H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 73.74, 81.34, 121.58, 128.43, 129.48, 132.29; GC–MS (%) 202 (100), 200 (24), 150 (8), 101 (13), 88 (10). Compound **2b**:[27] white solid; mp 182–184 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.31 (s, 6H, 2Me), 7.09 (d, J = 8.0 Hz, 4H, ArH), 7.36 (d, J = 8.0 Hz, 4H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.63, 73.45, 81.55, 118.80, 129.22, 132.40, 129.50; GC–MS (%) 230 (100), 215 (17), 115 (17), 101 (15). Compound **2c**:[28] white solid; mp 90–92 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, J = 6.8 Hz, 6H, 2Me), 1.27–1.38 (m, 8H, $4CH_2$), 1.53–1.66 (m, 4H, $2CH_2$), 2.60 (t, J = 7.6 Hz, 4H, $2CH_2$), 7.14 (d, J = 8.0 Hz, 4H, ArH), 7.43 (d, J = 8.0 Hz, 4H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 13.78, 22.29, 30.63, 31.21, 35.74, 73.27, 81.36, 118.77, 128.33, 132.19, 144.28; GC–MS (%) 342 (79), 285 (100), 228 (48). Compound **2d**: white solid; mp 214–216 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.92 (s, 6H, 2OMe), 7.09 (s, 2H, ArH), 7.16 (d, J = 9.0 Hz, 2H, ArH), 7.52 (d, J = 8.4 Hz, 2H, ArH), 7.68 (d, J = 8.4 Hz, 4H, ArH), 7.99 (s, 2H, ArH); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 55.16, 74.25, 82.51, 105.66, 116.46, 119.41, 126.73, 128.12, 128.96, 129.21, 132.55, 134.36, 158.51; GC–MS (%) 362 (100), 331 (76), 300 (46). Compound **2e**:[29] white solid, mp 60–62 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.55–1.67 (m, 8H, $4CH_2$), 2.11–2.14 (m, 8H, $4CH_2$), 6.25 (t, J = 4.0 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.3, 22.1, 25.8, 28.6, 71.5, 82.7, 119.9, 138.0, GC–MS (%): 210 (100) 181 (23), 167 (74), 153 (53), 128 (24), 115 (33), 91 (24), 77 (41). Compound **2f**:[30] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (t, J = 7.2 Hz, 6H, 2Me), 1.45–1.59 (m, 4H, $2CH_2$), 2.20 (t, J = 6.8 Hz, 4H, $2CH_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 13.22, 20.93, 21.61, 65.14; GC–MS (%) 134 (39), 119 (32), 105 (41), 91 (100), 78 (45), 63 (28). Compound **2g**:[17] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, J = 7.2 Hz, 6H, 2Me), 1.26–1.58 (m, 8H, $4CH_2$), 2.27 (t, J = 6.8 Hz, 4H, $2CH_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 13.29, 18.65, 21.68, 30.15, 65.00, 74.06; GC–MS (%) 162 (37), 147 (3), 133 (2), 119 (16), 91 (100), 78 (48). Compound **2h**:[29] Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (t, J = 7.6 Hz, 6H, 2Me); 1.28–1.54 (m, 12H, $6CH_2$), 2.25 (t, J = 7.2 Hz, 4H, $2CH_2$); 13C NMR (75.5 MHz, $CDCl_3$) δ 13.91, 19.23, 22.21, 28.04, 31.00, 65.21, 77.5; GC–MS (%) 190 (34), 161 (15), 105 (57), 91(100). Compound **2i**:[31] white solid; mp 106–108 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.17 (s, 18H, 6Me); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ -0.34, 89.99, 93.04. Compound **2j**:[18] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.40 (s, 6H, 2OMe), 4.17 (s, 4H, $2CH_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 57.60, 59.90, 70.24, 74.97.