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Ethynylation of pyrroles with 1-acyl-2-bromoacetylenes on alumina: a formal 'inverse Sonogashira coupling'

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Abstract—Pyrroles are cross-coupled with 1-acyl-2-bromoacetylenes on the surface of Al_2O_3 at room temperature under solvent-free conditions to afford 2-(acylethynyl)pyrroles with 100% regioselectivity and in good yields, thus representing the first example of a palladium-, copper-, base-, and solvent-free ('green') ethynylation of pyrroles, which can be considered a formal 'inverse Sonogashira coupling'. Given the interest in functionalized pyrroles and acetylenes, this new facile and environmentally friendly cross-coupling should be of significant interest for the role of acylhaloacetylenes in pyrrole and acetylene chemistry.
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Coupling of haloarenes and hetarenes with terminal acetylenes in the presence of palladium(0,II) complexes, copper halides and bases to furnish aryl- or hetarylacetylenes (Sonogashira coupling)[1] or its copper-free versions[2] and their numerous modifications[3] have attracted steady attention from the synthetic community since their publication. This coupling has grown in relevance in the development of efficient new syntheses of diverse building blocks, natural products, pharmaceuticals, and molecular materials for advanced technologies.[4]

A commonly recognized challenge in the Sonogashira coupling is the development of metal-free protocols and this is why a number of its copper-free versions employing amines[5] or ionic liquids[6] continue to be elaborated. A copper-free procedure without amine has also been reported.[7]

Recently,[8] a palladium- and copper-free version of the Sonogashira coupling was communicated, which described strongly basic phase-transfer conditions, actually constituting a nucleophilic aromatic substitution of iodine by acetylide anions. To obviate the environmental problems associated with the Sonogashira coupling, solventless protocols[9] utilizing the Pd–CuI–PPh_3/KF–Al_2O_3 catalytic systems and later[10] their microwave-enhanced variant have been proposed.

In spite of its general character, the Sonogashira coupling has not often been employed, if at all, in pyrrole chemistry, since the starting halogenated pyrroles are neither readily available nor stable, except for those possessing electron withdrawing substituents[11] (although a number of natural polyhalogenated pyrrole antibiotics are known[12]). Therefore, it would be of methodological importance to devise an inverse version of the Sonogashira coupling, in which nonhalogenated pyrroles could be cross-coupled with readily available halogenated acetylenes, for example, through straightforward halogenation of acetylenes in alkaline aqueous solutions.[13]

Our efforts to reach this goal have led us to the finding that pyrroles **1** can be smoothly coupled with 1-acyl-2-bromoacetylenes **2** on the surface of alumina to give 2-(acylethynyl)pyrroles **3** (Scheme 1).

The reaction proceeds at room temperature for 30–60 min and is a slightly exothermic (5–8 °C on a 0.5–1.0 mmol scale). Experimentally, the reactants are pulverized with a 10-fold mass excess of Al_2O_3 under solvent-free conditions, though some amounts of extragents (*n*-hexane, Et_2O) to take off the products from the reaction mixture are required.[14]

Keywords: Pyrroles; 1-Acyl-2-bromoacetylenes; Al_2O_3; 2-(Acylethynyl)-pyrroles; Sonogashira coupling.
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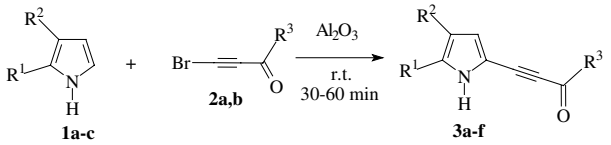


R^1 = H, R^2 = H (**a**) R^3 = Ph (**a**), 2-thienyl (**b**)
R^1-R^2 = $(CH_2)_4$ (**b**)
R^3 = Ph, R^2 = H (**c**)

3[a]	R^1	R^2	R^3	Yield, %[b]
a	H	H	Ph	55
b	$(CH_2)_4$		Ph	54
c	Ph	H	Ph	50
d	H	H	2-thienyl	70
e	$(CH_2)_4$		2-thienyl	60
f	Ph	H	2-thienyl	63

[a] 0.5-1.0 mmol of pyrrole, 0.5-1.0 mmol of alkyne, 10-fold mass excess of Al_2O_3, room temperature, 30-60 min.
[b] Isolated yieds.

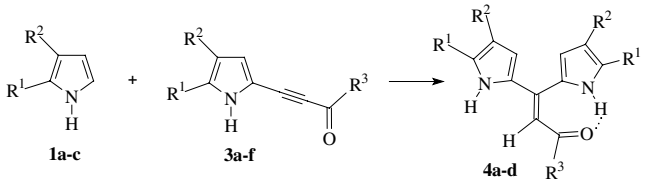
Scheme 1.

The reaction is 100% regioselective: no isomeric 1- or 3-(acylethynyl)pyrroles were detected in the reaction mixture (^{1}H NMR).[15] Side products of the coupling are 1,1-di(2-pyrrolyl)-2-acylethenes **4**, which are probably formed by the addition of pyrroles **1** to the major products **3** (Scheme 2).

The yields of **4** are normally up to 19%, expectedly, increasing, when excess pyrrole, higher temperatures or longer reaction times are employed. For example, reacting a 2-fold molar excess of pyrrole **1b** with acetylene **2b**, gave 55% and 35% yields of **3e** and **4d**, respectively (Scheme 2).

In the ^{1}H NMR spectra ($CDCl_3$) of **4a–d**, the NH protons of one pyrrole ring are shifted-downfield (13.80–14.96 ppm) compared to the other one (8.16–8.86 ppm), indicating its involvement in strong intramolecular H-bonding with the carbonyl group.

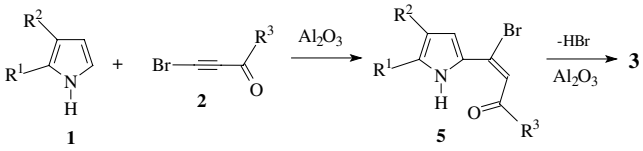
The mechanism of this new ethynylation is completely different from the true Sonogashira coupling and involves an addition–elimination sequence (Scheme 3), probably promoted by the coordinatively unsaturated center (electrophilic assistance) and by mechanoactivation (grinding up the reactants with Al_2O_3).



4[a]	R^1	R^2	R^3	Yield, %[b]
a	H	H	Ph	17
b	$(CH_2)_4$		Ph	19
c	Ph	H	Ph	39[c,d]
d	$(CH_2)_4$		2-thienyl	35[d]

[a] The products were isolated from the reactions of **1** with **2** (equimolar ratios; for the conditions, see Table 1).
[b] Isolated yields.
[c] The reaction time was 3 h. [d] 2-fold excess of **1**.

Scheme 2.



Scheme 3.

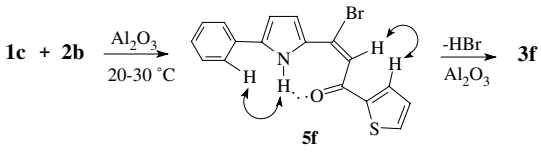
In fact, *E*-2-(1-bromo-2-thienoylethenyl)pyrroles **5f**, a possible intermediate (from the reaction of **1c** with **2b**), has been identified in the $CDCl_3$ extract of the reaction mixture by ^{1}H NMR (δ, ppm: 7.79–7.35, 5-phenyl, 5H; 6.76, H-4, 1H; 7.11, H-3, 1H; 7.84, 7.69, 7.18, thenoyl, 3H; 14.41, NH, 1H; 7.21, ethenyl, 1H) (Scheme 4).

The *E*-configuration of **5** was assigned by 2D COSY and NOESY techniques: interactions between the ethenyl proton and the H-3 thienoyl proton and the NH proton with the phenyl *ortho*-proton were detected. In **5**, as in the case of **4**, strong intramolecular H-bonding between the NH and C=O groups manifested itself by an anomalous downfield shift of the NH proton (14.41 ppm).

However, upon chromatography (Al_2O_3) of the reaction mixture 1 h after the reaction, the pyrrole **5f** was not discernable (^{1}H NMR) and the yield of the corresponding acetylenic pyrrole **3f** was 60%. If silica, instead of alumina, was employed as the reaction medium, the adducts **5** became the major products (the yield reaches 60%) and the ethynylpyrroles **3** were detectable (^{1}H NMR) as traces, only.

It is common knowledge that NH aromatic heterocycles,[16a] particularly pyrroles,[16b,c] add to acetylenes exclusively or mostly as *N*-centered nucleophiles. The experimental data from this work (Schemes 2 and 4) support our recent findings that alkyl-, aryl-, or hetarylpyrroles, when reacting with acetylenes activated by strong electron-withdrawing substituents, can add to the triple bond as *C*-centered nucleophiles.[17]

An attempt to effect the coupling of 1-bromophenylacetylene with pyrroles **1b**,**c** under the same conditions led to recovery of starting materials. This may imply that the reaction is probably limited to alkynes bearing a carbonyl functionality and other electron-withdrawing substituents, although a more systematic study is needed to finalize such a conclusion.



Scheme 4.

Given that alkyl-, aryl-, and hetarylpyrroles, as well as cycloalkenopyrroles are now readily available via the two-step reaction of ketones (through ketoximes) with acetylene (Trofimov reaction),[12,16c,18] and that bromoacetylenes can be easily prepared by bromination of terminal acetylenes,[13] the new coupling may become a useful economic and 'green' methodology in both pyrrole and acetylene chemistry.

In summary, we have devised a novel approach for the synthesis of 2-acylethynylpyrroles from pyrroles and 1-acyl-2-bromoacetylenes (in a manner resembling an 'inverse Sonogashira coupling') that is effected with high regioselectivity and in good yields under mild conditions: Al_2O_3, room temperature, 30–60 min, without palladium, copper, base, or solvent. Studies directed towards understanding the coupling mechanism, its scope and limitations are underway.

Acknowledgements

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14. Preparative procedure illustrating the preparation of 2-(acylethynyl)pyrroles **3**. Equimolar amounts (0.5–1.0 mmol) of pyrrole **1** and a 1-acyl-2-bromoacetylene **2** were ground together at rt with a 10-fold amount (by weight) of Al_2O_3 (chromatography grade, washed with distilled water and ethanol and dried until constant weight) in a china mortar and pestle for 1–2 min. The reaction mixture self-heated (5–8 °C) and within 10 min turned from yellow to orange-brown. After 30–60 min, the reaction products were extracted sequentially with *n*-hexane (10–15 mL), *n*-hexane–Et_2O (2:1–1:2) (40–50 mL) and Et_2O (15–20 mL). The fractions were further chromatographed on a column or in thin layer (Al_2O_3) to yield pyrroles **3** as air stable yellow-orange needles (after recrystallization from *n*-hexane–Et_2O, 1:1), and 1,1-di(pyrrol-2-yl)-2-acylethenes **4**.
2-(Benzoylethynyl)pyrrole—**3a**: yellow crystals, mp 141–142 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$); δ 8.89 (br s, 1H), 8.19 (m, 2H), 7.63 (m, 1H), 7.51 (m, 2H), 7.00 (m, 1H), 6.90 (m, 1H), 6.33 (m, 1H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 177.99, 136.81, 133.97, 129.43, 128.63, 123.91, 120.91, 110.72, 110.05, 92.15, 89.02. IR (KBr, cm^{-1}): 3217, 3113, 3084, 2168, 1604, 1571, 1549, 1449, 1421, 1398, 1320, 1305, 1264, 1238, 1175, 1142, 1048, 1031, 1018, 947, 933, 883, 834, 791, 742, 696, 655, 598. Anal. Calcd for $C_{13}H_9NO$: C, 79.98; H, 4.65; N, 7.17. Found: C, 79.88; H, 4.78; N, 6.99.
2-(Benzoylethynyl)-4,5,6,7-tetrahydroindole—**3b**: yellow-orange crystals, mp 167–168 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 8.24 (br s, 1H), 8.13 (m, 2H), 7.56 (m, 1H), 7.46 (m, 2H), 6.61 (d, ^4J = 1.8 Hz, 1H), 2.59 (m, 2H), 2.49 (m, 2H), 1.79 (m, 2H), 1.74 (m, 2H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 177.63, 137.14, 134.82, 133.62, 129.31, 128.55, 120.33, 120.29, 107.83, 93.62, 91.15, 23.41, 23.21, 22.89, 22.71. IR (KBr, cm^{-1}): 3280, 3065, 2948, 2920, 2839, 2155,

1612, 1596, 1567, 1468, 1434, 1365, 1316, 1250, 1224, 1164, 1139, 1042, 1022, 930, 824, 806, 787, 692, 633. Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.56; H, 6.20; N, 5.78.

2-(Benzoylethynyl)-5-phenylpyrrole—**3c**: orange crystals, mp 182–183 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 9.04 (br s, 1H), 8.22 (m, 2H), 7.65 (m, 1H), 7.59 (m, 2H), 7.56 (m, 2H), 7.46 (m, 2H), 7.35 (m, 1H), 6.97 (dd, ^3J = 3.6 Hz, ^4J = 2.5 Hz, 1H), 6.62 (dd, ^3J = 3.6 Hz, ^4J = 2.8 Hz, 1H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 177.62, 137.50, 136.75, 133.80, 130.85, 129.32, 129.07, 128.50, 127.88,124.62, 122.54, 110.72, 108.24, 93.24, 89.12. IR (KBr, cm^{-1}): 3309, 3061, 2166, 1628, 1605, 1596, 1574, 1538, 1509, 1475, 1456, 1382, 1315, 1291, 1245, 1218, 1172, 1075, 1042, 1022, 968, 901, 792, 759, 685, 650. Anal. Calcd for $C_{19}H_{13}NO$: C, 84.11; H, 4.83; N, 5.16. Found: C, 83.75; H, 5.09; N, 5.51.

2-(Thienoylethynyl)pyrrole—**3d**: yellow crystals, mp 143–144 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 8.93 (br s, 1H), 7.92 (dd, ^3J = 3.9 Hz, ^4J = 1.2 Hz, 1H), 7.67 (dd, ^3J = 4.9 Hz, ^4J = 1.2 Hz, 1H), 7.14 (dd, ^3J = 4.9 Hz, ^3J = 3.9 Hz, 1H), 6.96 (m, 1H), 6.83 (m, 1H), 6.28 (m, 1H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 169.71, 144.82, 134.84, 134.66, 128.36, 123.68, 120.77, 110.78, 110.03, 91.34, 87.05. IR (KBr, cm^{-1}): 3167, 3096, 3071, 3004, 2174, 1581, 1555, 1512, 1433, 1409, 1353, 1320, 1266, 1249, 1140, 1099, 1079, 1061, 1039, 996, 929, 883, 858, 820, 749, 728, 655, 598. Anal. Calcd for $C_{11}H_7NOS$: C, 65.65; H, 3.51; N, 6.96; S, 15.93. Found: C, 65.80; H, 3.31; N, 6.57; S, 15.66.

2-(Thienoylethynyl)-4,5,6,7-tetrahydroindole—**3e**: dark-yellow crystals, mp 147–148 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 8.43 (br s, 1H), 7.87 (dd, ^3J = 3.7 Hz, ^4J = 1.2 Hz, 1H), 7.63 (dd, ^3J = 4.9 Hz, ^4J = 1.2 Hz, 1H), 7.11 (dd, ^3J = 4.9 Hz, ^3J = 3.7 Hz, 1H), 6.58 (d, ^4J = 2.0 Hz, 1H), 2.57 (m, 2H), 2.48 (m, 2H), 1.76 (m, 4H). ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 169.56, 145.09, 134.83, 134.21, 128.23, 120.24, 120.17, 107.60, 92.72, 89.82, 23.36, 23.15, 22.84, 22.67. IR (KBr, cm^{-1}): 3260, 3102, 3065, 2944, 2918, 2842, 2153, 1596, 1569, 1513, 1469, 1410, 1351, 1316, 1255, 1227, 1137, 1081, 1051, 1016, 943, 858, 823, 806, 760, 714, 667, 630. Anal. Calcd for $C_{15}H_{13}NOS$: C, 70.56; H, 5.13; N, 5.48; S, 12.56. Found: C, 70.52; H, 5.48; N, 5.49; S, 12.90.

2-(Thienoylethynyl)-5-phenylpyrrole—**3f**: red-orange crystals, mp 183–184 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 9.04 (br s, 1H), 7.95 (dd, ^3J = 3.7 Hz, ^4J = 1.2 Hz, 1H), 7.68 (dd, ^3J = 4.9 Hz, ^4J = 1.2 Hz, 1H), 7.58–7.31 (m, 5H), 7.17 (dd, ^3J = 4.9 Hz, ^3J = 3.7 Hz, 1H), 6.90 (dd,^3J = 3.6 Hz, ^4J = 2.2 Hz, 1H), 6.57 (dd, ^3J = 3.6 Hz, ^4J = 2.4 Hz, 1H). IR (KBr, cm^{-1}): 3298, 3066, 2169, 1597, 1558, 1512, 1462, 1406, 1354, 1315, 1302, 1245, 1225, 1194, 1057, 1044, 1022, 942, 919, 860, 784, 755, 724, 691, 652. Anal. Calcd for $C_{17}H_{11}NOS$: C, 73.62; H, 4.00; N, 5.05; S, 11.56. Found: C, 73.51; H, 4.26; N, 5.16; S, 11.70.

1,1-Di(pyrrol-2-yl)-2-benzoylethene—**4a**: red-orange oil. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 13.99 (br s, 1H), 8.67 (br s, 1H), 7.98 (m, 2H), 7.52 (m, 1H), 7.47 (m, 2H), 7.15 (m, 1H), 6.95 (m, 1H), 6.84 (s, 1H), 6.73 (m, 2H), 6.38 (m, 1H), 6.33 (m, 1H). Anal. Calcd for $C_{17}H_{14}N_2O$: C, 77.84, H, 5.38, N, 10.68. Found: C, 77.46; H, 5.49; N, 10.32.

1,1-Di(4,5,6,7-tetrahydroindol-2-yl)-2-benzoylethene—**4b**: red crystals, mp 186–187 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 14.00 (br s, 1H), 8.25 (br s, 1H), 7.97 (m, 2H), 7.50 (m, 1H), 7.48 (m, 2H), 6.65 (s, 1H), 6.62 (d, ^4J = 2.0 Hz, 1H), 6.50 (d, ^4J = 2.2 Hz, 1H), 2.81 (m, 2H), 2.68 (m, 2H), 2.60 (m, 2H), 2.58 (m, 2H), 1.84 (m, 8H). Anal. Calcd for $C_{25}H_{26}N_2O$: C, 81.05; H, 7.07; N, 7.56. Found: C, 81.38; H, 7.45; N, 7.30.

1,1-Di(5-phenylpyrrol-2-yl)-2-benzoylethene—**4c**: red crystals, mp 204–205 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 14.96 (br s, 1H), 8.86 (br s, 1H), 8.06 (m, 2H), 7.87–7.31 (m, 5H), 7.57–7.29 (m, 5H), 7.53 (m, 1H), 7.48 (m, 2H), 6.95 (m, 1H), 6.89 (s, 1H), 6.83 (m, 1H), 6.81 (m, 1H), 6.67 (m, 1H). Anal. Calcd for $C_{29}H_{22}N_2O$: C, 84.03; H, 5.35; N, 6.76. Found: C, 83.78; H, 5.67; N, 6.60.

1,1-Di(4,5,6,7-tetrahydroindol-2-yl)-2-thienoylethene—**4d**: dark-red crystals, mp 210 °C. ^{1}H NMR (250.13 MHz, $CDCl_3$) δ 13.80 (br s, 1H), 8.16 (br s, 1H), 7.71 (dd, ^3J = 3.7 Hz, ^4J = 1.2 Hz, 1H), 7.51 (dd, ^3J = 4.9 Hz, ^4J = 1.2 Hz, 1H), 7.08 (dd, ^3J = 4.9 Hz, ^3J = 3.7 Hz, 1H), 6.57 (d, ^4J = 2.2 Hz, 1H), 6.56 (s, 1H), 6.44 (d, ^4J = 2.4 Hz, 1H), 2.75 (m, 2H), 2.64 (m, 2H), 2.54 (m, 4H), 1.80 (m, 8H). Anal. Calcd for $C_{23}H_{24}N_2OS$: C, 73.37; H, 6.42; N, 7.44; S 8.52. Found: C, 72.99; H, 6.64; N, 7.58; S, 8.86.

15. Amidation of 1-bromo-2-phenylacetylene with the two vinylogous amides, 2,4-dimethyl-3-acetylpyrrole and 3-benzoylpyrrole (10 mol% $CuSO_4 \cdot H_2O$, 20 mol% 1,10-phenanthroline, 2.0 equiv of K_3PO_4, toluene, 70–80 °C, 18–36 h) gave only 1-(2-phenylethynyl)pyrroles in 50% and 71% yields, respectively, see: Zhang, Y.; Hsung, R. P.; Tracey, M. R.; Kurtz, K. C. M.; Vera, E. L. *Org. Lett.* **2004**, *6*, 1151–1154.
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