Push-Pull Ynamines via Alkynyliodonium Chemistry

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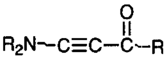
The reaction of substituted alkynyl(phenyl)iodonium salts **3a–e** with lithium diphenylamine ($LiNPh_2$) leading to the formation of push-pull ynamine products **5a–e** is described.

There has been a resurgence of interest in acetylene chemistry in general and, in particular, in functionalized acetylenes.[1,2] Of special interest are the functionalized acetylenes containing push-pull systems **1**, with electron-donating groups (EDG) at one end and electron-withdrawing (EWG) substituents at the opposite end of the triple bond. The most commonly employed electron-donating groups are the dialkyl or diaryl amino functionalities whereas the electron-withdrawing groups tend to be carbonyl or cyano, giving rise to push-pull ynamines **2**. A variety of methods has been developed[3–6] over the years for the formation of the push-pull ynamine systems **2**. Many of these rely upon elimination (dehydrohalogenation or dehalogenation) or nucleophilic processes with inherent limitations. In this paper we wish to report a new, mild methodology for the formation of push-pull ynamines **2** via alkynyliodonium chemistry.[7]

$EDG \longrightarrow C{\equiv}C \longrightarrow EWG$

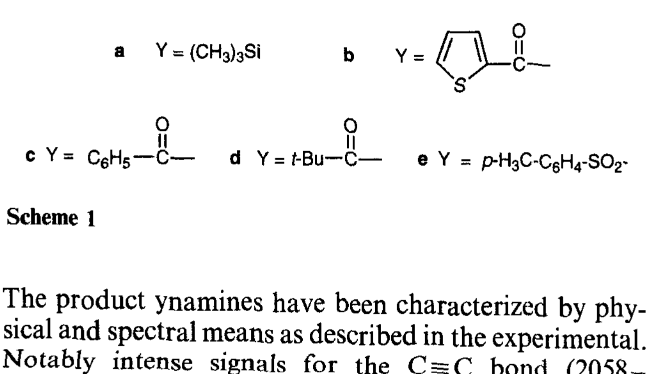
1



$R_2N{-}C{\equiv}C{-}\overset{O}{\overset{\|}{C}}{-}R'$

2

Diverse β-functionalized alkynyl(phenyl)iodonium triflates **3** are readily available[8] and, upon interaction with lithium diphenylamine ($LiNPh_2$) in diethyl ether followed by workup, result in the desired bis-functionalized push-pull alkynes **5** in reasonable (43–66%) isolated yields (Scheme 1). This methodology is readily applicable for the preparation of a variety of carbonyl functionalized ynamines, as well as the silyl substituted systems and most importantly the hitherto unknown sulfone substituted molecule **5e**.



Scheme 1

The product ynamines have been characterized by physical and spectral means as described in the experimental. Notably intense signals for the C≡C bond (2058–2250 cm^{-1}) were observed, as well as for the carbonyl and sulfone functionalities in the infrared. The ^1H and ^{13}C NMR are all in accord with the proposed structures, the sp carbons in the ^{13}C NMR between 73.4 and 114.2 ppm being especially indicative.

In summary, a new, mild method of push-pull acetylene preparation via an alkynyliodonium species which is tolerant of a variety of functionalities is reported.

Melting points (uncorrected) were obtained with a Mel-Temp® capillary melting point apparatus. Radial chromatography was performed with a Harrison Research Chromatotron®, model 7924T. Infrared spectra were recorded neat or as CCl_4 mulls on a Mattson FT-IR spectrometer. All NMR spectra were recorded on a Unity 300 Varian spectrometer. The ^1H NMR spectra were recorded at 300 MHz, and chemical shifts are reported relative to $CDCl_3$ (δ 7.24), CD_2Cl_2 (δ 5.32) or CD_3CN (δ 1.93). The ^{13}C NMR spectra were recorded at 75 MHz, ^1H decoupled, and reported relative to $CDCl_3$ (δ 77.0), CD_2Cl_2 (δ 53.8) or CD_3CN (δ 1.30). Mass spectra were obtained with either a Finnigan MAT 90 mass spectrometer with a Finnigan MAT ICIS II operating system or a VG Micromass 7050E double focusing high resolution mass spectrometer with the VG data system 2000 under electron impact (EI) at 70 eV. 3-Nitrobenzyl alcohol was used as a matrix in CH_2Cl_2, $CHCl_3$, or CH_3CN as solvent. Polypropylene glycol was used as a reference for peak matching. Microanalyses were performed by Atlantic Microlab Inc. Norcross, Georgia. All commercial reagents were ACS reagent grade and used without further purification. Silica gel (200–400 mesh) was purchased from Baxter Scientific. Silica gel 60 (containing gypsum) for Chromatotron plates was purchased from EM Science. Reagent grade CH_2Cl_2, hexanes, and CH_3CN were dried by distillation over CaH_2. Et_2O was distilled from Na/benzophenone. Reaction flasks were flame dried and flushed with N_2 prior to use. The syntheses of alkynyliodonium triflates have been previously reported.[8] Satisfactory microanalysis results were obtained for **5b**: C + 0.23, H + 0.19, N − 0.11, S − 0.14.

N,N-Diphenylamino(trimethylsilyl)acetylene (5a):

To a stirred solution of diphenylamine (1.35 g, 3.00 mmol) in Et_2O (50 mL), BuLi (1.23 mL, 2.5 M, 3.00 mmol) was added at −78 °C under N_2. The trimethylsilylethynyl(phenyl)iodonium triflate (0.500 g, 1.00 mmol) was then added all at once and the reaction mixture was stirred for 3 h while slowly warming to 20 °C. The reaction mixture was then eluted through silica gel (2.0 g) with CH_2Cl_2 and the volume reduced on a rotary evaporator. Silica gel radial chromatography (200–400 mesh, 2 mm plate, CH_2Cl_2) and removal of the solvent by rotary evaporation afforded *N,N*-diphenylamino(trimethylsilyl)acetylene as a red oil; yield: 0.34 g (43%).

IR (neat): ν = 3062, 2959, 2058, 1734, 1590, 1471 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.68 (d, 4H, J = 7.5 Hz), 7.31 (t, 2H, J = 7.5 Hz), 7.09 (t, 4H, J = 6.9 Hz), 0.18 (s, 9H).

^{13}C NMR ($CDCl_3$): δ = 137.4, 130.2, 127.4, 104.1, 94.3, 85.9, 0.14.

HRMS (FAB) (Calc. for $C_{17}H_{19}NSi$): m/z = 265.1287 (M^+). Found: 265.1283.

***N,N*-Diphenylamino(2-thiophenecarbonyl)acetylene (5b):**

To a stirred solution of diphenylamine (0.173 g, 1.00 mmol) in Et_2O (50 mL), BuLi (0.41 mL, 2.5 M, 1.0 mmol) was added at −78 °C under N_2. The 2-thiophenecarbonylethynyl(phenyl)iodonium triflate (0.500 g, 1.00 mmol) was added all at once and the solution was stirred for 5 min. The reaction mixture was then eluted through silica gel with CH_2Cl_2 and the volume reduced on a rotary evaporator. Silica gel radial chromatography (200–400 mesh, 2 mm plate, CH_2Cl_2) and removal of the solvent by rotary evaporation afforded *N,N*-diphenylamino(2-thiophenecarbonyl)acetylene as a red oil; yield: 0.16 g (53%).

IR (neat): ν = 3054, 2986, 2187, 1592, 1490, 1452, 1350, 1234, 1191, 1048, 931 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 7.72 (d, 1 H, J = 3.8 Hz), 7.63 (d, 1 H, J = 4.8 Hz), 7.42 (m, 8 H), 7.29 (t, 2 H), 7.13 (t, 1 H, J = 4.4 Hz).

^{13}C NMR (CDCl$_3$): δ = 169.3, 145.8, 142.1, 133.5, 133.1, 130.1, 128.4, 126.5, 122.3, 97.1, 73.9.

Benzoyl(*N*,*N*-diphenylamino)acetylene (5c):

To a stirred solution of diphenylamine (0.51 g, 3.0 mmol) of Et$_2$O (40 mL), BuLi (1.2 mL, 2.5 M, 3.0 mmol) was added at −78 °C under N$_2$. The benzoylethynyl(phenyl)iodonium triflate (1.44 g, 3.00 mmol) was added all at once and the solution was stirred for 1 h. The reaction was eluted through silica gel with CH$_2$Cl$_2$ and the volume reduced on a rotary evaporator. Silica gel radial chromatography (200–400 mesh, 2 mm plate, CH$_2$Cl$_2$) and removal of the solvent by rotary evaporation afforded 0.16 g (66 %) of benzoyl(*N*,*N*-diphenylamino)acetylene as a red oil; yield: 0.16 g (66 %).

IR (neat): ν = 302, 2171, 1572, 1507, 1470, 1438, 1308, 1155, 1014, 990 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 8.02 (m), 7.85 (m).

^{13}C NMR (CDCl$_3$): δ = 176.8, 141.9, 137.5, 132.9, 129.7, 128.9, 128.4, 126.0, 121.8, 98.3, 74.5.

HRMS (FAB) (calc. for C$_{21}$H$_{15}$ON): m/z = 297.1154. Found: 299.1166 (M$^+$).

2,2-Dimethylpropanoyl(*N*,*N*-diphenylamino)acetylene (5d):

To a stirred solution of diphenylamine (0.366 g, 2.16 mmol) in Et$_2$O (50 mL), BuLi (0.87 mL, 2.5 M, 2.16 mmol) was added at −78 °C under N$_2$. The 2,2-dimethylpropanoylethynyl(phenyl)iodonium triflate (1.00 g, 2.16 mmol) was added all at once and the solution was stirred for 1 h. The reaction was eluted through silica gel with CH$_2$Cl$_2$ and the volume reduced on a rotary evaporator. Silica gel radial chromatography (200–400 mesh, 2 mm plate, CH$_2$Cl$_2$) and removal of the solvent by rotary evaporation afforded 0.38 g (63 %) of 2,2-dimethylpropanoyl(*N*,*N*-diphenylamino)acetylene as a red oil; yield: 0.38 g (63 %).

IR (neat): ν = 3043, 2181, 1459, 1378, 1080, 996 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 7.40 (t), 7.31 (d), 7.23 (t) 1.22 (s).

^{13}C NMR (CDCl$_3$): δ = 193.3, 142.6, 130.1, 126.3, 122.1, 97.2, 73.5, 44.4, 27.0.

HRMS (FAB) (calc. for C$_{19}$H$_{19}$ON): m/z = 277.1466. Found: 277.1437 (M$^+$).

***N*,*N*-Diphenylamino(*p*-toluenesulfonyl)acetylene (5e):**

To a stirred solution of phenyl(*p*-toluenesulfonylethynyl)iodonium triflate (0.250 g, 0.47 mmol) in CH$_3$CN (50 mL), sodium diphenylamine (0.090 g, 0.47 mmol) was aded at −45 °C under N$_2$ and the reaction was stirred for 5 min. The reaction mixture was warmed to 20 °C and the volume reduced on a rotary evaporator. The resultant solid was dissolved in CH$_2$Cl$_2$ (10 mL) and filtered to remove the sodium triflate. Addition of hexane (10 mL) afforded *N*,*N*-diphenylamino(*p*-toluenesulfonyl)acetylene as a red solid; yield: 0.093 g (57 %).

IR (neat): ν = 2197, 1671, 1666, 1492, 1290, 1030 cm^{-1}.

^{1}H NMR (CDCl$_3$): δ = 7.87 (t), 7.72 (t), 7.25 (m), 6.80 (d), 2.44 (s).

^{13}C NMR (CDCl$_3$): δ = 147.2, 143.7, 136.2, 133.8, 133.4, 130.8, 129.5, 127.4, 114.2, 103.4, 22.1.

HRMS (FAB): (calc. for C$_{21}$H$_{17}$SO$_2$N): m/z = 347.0914. Found: 347.0980 (M$^+$).

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