Bis(phenyliodonium) Diyne Triflates $PhIC{\equiv}C(p\text{-}C_6H_4)_nC{\equiv}CIPh \bullet 2OTf$ and $PhIC{\equiv}C(CH_2)_nC{\equiv}CIPh \bullet 2OTf$: Preparation, Characterization, and Reaction with Triphenylphosphine†

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Bis(phenyliodonium) diyne triflates 8–10 were prepared by the reaction of the corresponding tributyltin substituted diacetylenes 4–6 with cyanophenyliodonium triflate 7 in 78–93% yields as relatively stable microcrystalline solids. They were characterized by multinuclear NMR, IR, and analytical data. Iodonium salts 8–10 reacted with triphenylphosphine under mild conditions with the loss of iodobenzene giving bisphosphonium salts 11,12 in high yields.

The carbon–carbon triple bond represents one of the oldest and most versatile functionalities in organic chemistry. Particularly interesting are molecules with more than one triple bond. Members of this family are of considerable current research activity in the areas of nonlinear optics[1] and organic conductors[2] as well as new types of antitumor antibiotics.[3] Despite active interest in this class of alkynes little is known about simple functionalized diynes that might serve as precursors to the above group of materials and compounds as well as other potentially useful transformations.

Recently, alkynyliodonium salts,[4] **1**, the latest members of the family of tricoordinate iodine(III) species,[5] have emerged as particularly useful reagents for the preparation of a variety of monofunctionalized acetylenes[6] and other interesting transformations.[7,8] Particularly intriguing are the bis(phenyliodonio)acetylene **2**[9] and -diacetylene **3**[9a] that serve as novel C_2- and C_4-transfer agents. Unfortunately, the considerable instability of **3** limits its widespread application. Hence, we looked for (a) means of stabilizing such conjugated bisiodonium diynes and (b) extension to nonconjugated bisiodonium diynes.

$$\underset{\mathbf{1}}{RC{\equiv}CI^{+}Ph\ X^{-}} \qquad \underset{\mathbf{2}}{PhI^{+}C{\equiv}CI^{+}Ph{\cdot}2^{-}OTf}$$

$$\underset{\mathbf{3}}{PhI^{+}C{\equiv}C{-}C{\equiv}CI^{+}Ph{\cdot}2^{-}OTf}$$

In this paper we report the preparation, characterization, and some chemical properties of two new types of bis(iodonium) diynes: (a) conjugated, phenylene bridged, systems **8** and (b) various CH_2 as well as an O-bridged systems **9,10**.

Results and Discussion

Compounds **8–10** can be prepared by our iodonium-transfer process[9,10] starting from cyanophenyliodonium triflate **7** as the transfer agent and the appropriate alkynylstannanes **4–6** (Scheme I). Addition of a CH_2Cl_2 solution of the bistin diacetylene to a stirred suspension of reagent **7** under N_2 at −78 °C with subsequent warming to room temperature results in the rapid formation of a microcrystalline precipitate. Addition of hexanes to complete crystallization followed by filtration under N_2 and washing with dry hexanes affords the corresponding bis(iodonium) salts **8–10** in 78–93% yield. Phenylene derivatives **8a,b** are isolated in the form of pale yellow solids, and compound **8a** is relatively stable whereas **8b** decomposes in a few hours at room temperature. Compounds **9a–c**, where the two triple bonds are separated by an alkyl chain, are stable white solids which can be stored without decomposition for several weeks at room temperature or for extended periods in a refrigerator. Iodonium salt **10** containing the ether moiety in its structure turns into an oil at room temperature and is substantially less stable compared with **9**.

Bis(iodonium) salts **8–10** are fully characterized by multinuclear NMR, IR, and high-resolution mass spectra, and where stable, by microanalysis. Specifically, in the high-resolution FAB mass spectra the expected molecular peaks $(M - TfO^{-})^{+}$ of the monocationic part of salts **8–10** are observed. In the IR spectra very characteristic intense absorptions for the carbon–carbon triple bonds are observed at 2176–2192 cm^{-1}. The ^1H NMR displays the expected 2:1:2 aromatic resonances between δ 7.6 and 8.3

† Dedicated to Professor Andrew Streitwieser, Jr., on the occasion of his 65th birthday.

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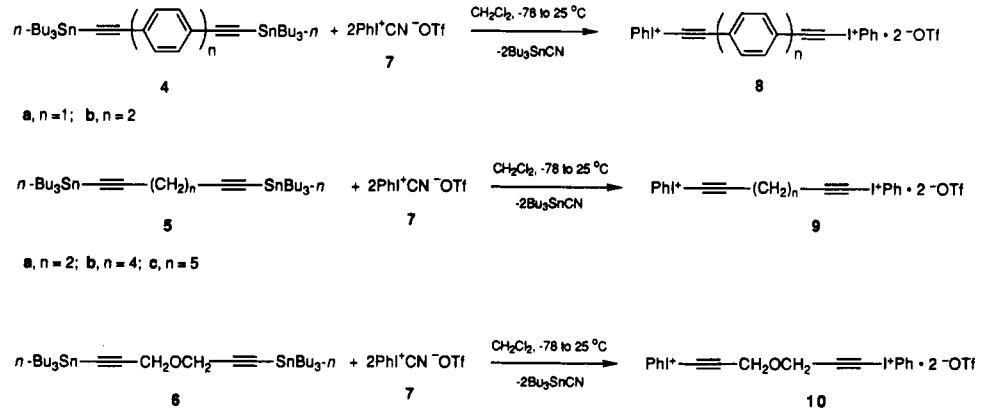
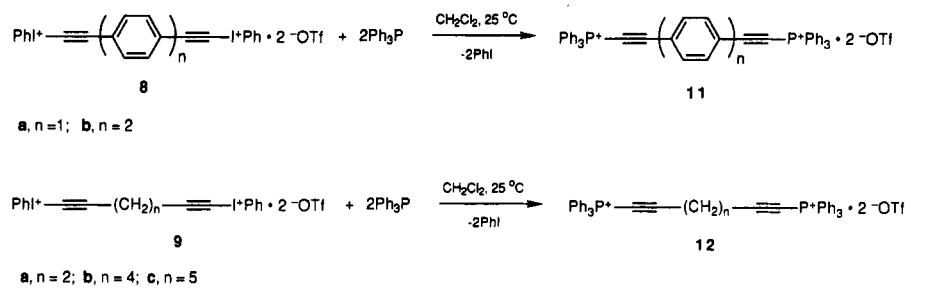
Scheme I



Scheme II



ppm typical of phenyliodonium salts as well as further characteristic patterns. The ^{13}C NMR spectra are all consistent with the proposed structures; specifically, signals for the acetylenic carbons are located at δ 21–36 ppm for the α-carbon and δ 104–111 ppm for the β-carbon which is typical of alkynyliodonium salts.[4] The presence of the triflate anion in **8–10** is confirmed by ^{19}F NMR.

Similar to the behavior of iodonium salts **1–3**,[4] bis(iodonium) triflates **8–10** are expected to be reactive toward nucleophiles. Particularly interesting are reactions of alkynyliodonium salts with triphenylphosphine resulting in alkynylphosphonium salts as the major products,[9,11] which are valuable Michael acceptors and precursors to synthetically useful substituted vinylphosphonium species.[11]

We examined the reactions of the relatively stable and crystalline salts **8a,b** and **10a–c** with triphenylphosphine in CH_2Cl_2 (Scheme II). The reactions (Scheme II) are complete in under an hour at room temperature and give the corresponding diphosphonium salts **11,12** in 67–90% yield as well as the expected iodobenzene. Phosphonium salts **11,12** are isolated from the reaction mixture as yellow hygroscopic oils or solids and are fully characterized by multinuclear NMR, IR, and high-resolution mass spectra. The high-resolution FAB mass spectra in all cases display the expected molecular peaks $(M - TfO^-)^+$ of the monocationic part of salts **11,12**. In the IR spectra, intense carbon–carbon triple bond signals are observed at 2205–2171 cm^{-1}. In the ^{31}P NMR, singlets at δ 6–8 ppm indicate the presence of an acetylenic phosphonium species.[12] The ^1H NMR and ^{13}C NMR spectra are all consistent with the proposed structures; signals for the acetylenic carbons are located at δ 62–73 ppm for the α-carbon and δ 125–126 ppm for the β-carbon with C–P coupling constants of 189–190 and 30–31 Hz, respectively. The presence of the triflate anion in **11,12** is confirmed by ^{19}F NMR.

In conclusion, bisalkynyl bis(phenyliodonium) triflates **(8–10)** can be prepared by the reaction of the corresponding tributyltin-substituted diacetylenes **(4–6)** with cyanophenyliodonium triflate **7** in high isolated yields as relatively stable microcrystalline solids. Iodonium salts **8–10** react with triphenylphosphine under mild conditions with the loss of iodobenzene and the formation of novel bisphosphonium salts **11,12** in high yields. We believe that these readily available, new, bis(iodonio)dialkynes will serve as useful precursors for a variety of transformations involving diynes.

Experimental Section

General Methods. Melting points (uncorrected) were obtained with a Mel-Temp capillary melting point apparatus. Infrared spectra were recorded on a Mattson FT-IR spectrophotometer. NMR spectra were recorded on a Varian XL 300 spectrometer at 300 (^1H NMR), 75 (^{13}C NMR), 121 (^{31}P NMR), and 282 MHz (^{19}F NMR). Chemical shifts for ^1H and ^{13}C NMR are reported in parts per million (ppm) relative to internal tetramethylsilane or the proton resonance due to the residual protons in the deuteriated NMR solvent; the chemical shifts for ^{19}F and ^{31}P NMR are relative to external $CFCl_3$ and 85% H_3PO_4, respectively. Mass spectra were obtained with a VG Micromass 7050E double focusing high-resolution mass spectrometer with the VG data system 2000 under positive ion fast atom bombardment (FAB) conditions at 8 keV. 3-Nitrobenzyl alcohol was used as a matrix in CH_2Cl_2 or $CHCl_3$ as solvent, and polypropylene glycol was used as a reference for peak matching. Microanalysis were performed by Atlantic Microlab Inc, Norcross, GA.

Materials. All commercial reagents were ACS reagent grade and used without further purification. [Cyano[(trifluoromethanesulfonyl)oxy]iodo]benzene **7** was prepared from iodosobenzene, trimethylsilyl triflate, and trimethylsilyl cyanide by a known procedure.[9b,13] Bis(tributyltin)diacetylenes **4–6** were prepared by a known method[14,15] from the corresponding di-

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acetylenes, *n*-butyllithium, and tributyltin chloride. 1,5-Hexadiyne, 1,7-octadiyne, and 1,8-nonadiyne were purchased from Aldrich and 1,4-diethynylbenzene purchased from Farchan. 4,4′-Diethynylbiphenyl was prepared by the method of Wright,[15] bis(propargyl) ether was synthesized by a known procedure.[16] All solvents used were dried by distillation over CaH_2. The reaction flasks were flame-dried and flushed with nitrogen.

General Procedure for Synthesis of Bis(alkynyl) Bis(phenyliodonium) Triflates. A solution of the appropriate bis(tributyltin)diacetylene **4–6** (5 mmol) in CH_2Cl_2 (20 mL) was added to a stirred suspension of reagent **7** (3.79 g, 10 mmol) in CH_2Cl_2 (100 mL) at −78 °C under nitrogen. The mixture was allowed to warm to 0 °C and stirred for 10 min until the formation of a white microcrystalline precipitate. Hexane was added to complete precipitation, and the solid was filtered under nitrogen, washed with dry hexane (100 mL), and dried in vacuo. Analytically pure materials were obtained by recrystallization from a concentrated solution of the iodonium salt in CH_3CN by addition of CH_2Cl_2 and ether.

1,4-Bis[[phenyl[(trifluoromethanesulfonyl)oxy]iodo]ethynyl]benzene (8a). Reaction of 1,4-bis[(tributylstannyl)ethynyl]benzene (**4a**) (3.27 g, 4.65 mmol) with reagent **7** (3.52 g, 9.30 mmol) gave 3.18 g (82%) of **8a** as a pale yellow microcrystalline solid, mp 144–146 °C dec: IR (CCl_4) 3082, 3064, 2176 (C≡C), 1298, 1218, 1157, 1022 cm^{-1}; ^1H NMR (CD_3CN) δ 8.21 (d, J = 8.2 Hz, 4 H), 7.76 (t, J = 8.0 Hz, 2 H), 7.61 (t, J = 8.1 Hz, 4 H), 7.58 (s, 4 H); ^{19}F NMR (CD_3CN) δ −78.65 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 135.7, 134.0, 133.9, 133.4, 122.9, 117.7 (all Ar), 121.1 (q, J = 318 Hz, $CF_3SO_3^-$), 105.3 ($C{\equiv}CI^+$), 36.4 ($C{\equiv}CI^+$); FAB HRMS m/z 680.869 119 ($M - CF_3SO_3^-$)$^+$, calcd for $C_{23}H_{14}F_3I_2O_3S$ 680.870 280. Anal. Calcd for $C_{24}H_{14}F_6I_2O_6S_2$: C, 34.72; H, 1.70; S, 7.72. Found: C, 34.71; H, 1.68; S, 7.76.

4,4′-Bis[[phenyl[(trifluoromethanesulfonyl)oxy]iodo]ethynyl]biphenyl (8b). Reaction of 1,4-bis[(tributylstannyl)ethynyl]biphenyl (**4b**) (3.90 g, 5.0 mmol) with reagent **7** (3.79 g, 10.0 mmol) gave 4.17 g (92%) of **8b** as a pale yellow microcrystalline solid, mp 85–86 °C dec: IR (CCl_4) 3082, 3068, 2171 (C≡C), 1288, 1243, 1173, 1021 cm^{-1}; ^1H NMR (DMSO-d_6/$CDCl_3$) δ 8.23 (d, J = 7.8 Hz, 4 H), 7.56–7.76 (m, 14 H); ^{19}F NMR (CD_3CN) δ −78.39 (s, $CF_3SO_3^-$); ^{13}C NMR (DMSO-d_6/$CDCl_3$) δ 141.3, 134.1, 133.1, 132.1, 131.8, 127.0, 119.2, 118.3 (all Ar), 121.1 (q, J = 318 Hz, $CF_3SO_3^-$), 103.3 ($C{\equiv}CI^+$), 40.0 ($C{\equiv}CI^+$). Anal. Calcd for $C_{30}H_{18}F_6I_2O_6S_2$: C, 39.75; H, 1.99; S, 7.07. Found: C, 39.03; H, 2.25; S, 6.94.

1,6-Bis[phenyl[(trifluoromethanesulfonyl)oxy]iodo]-1,5-hexadiyne (9a). Reaction of 1,6-bis(tributylstannyl)-1,5-hexadiyne (**5a**) (1.90 g, 2.90 mmol) with reagent **7** (2.20 g, 5.80 mmol) gave 2.05 g (90%) of **9a** as a white microcrystalline solid, mp 141–143 °C dec: IR (CCl_4) 3084, 2927, 2192 (C≡C), 1291, 1211, 1177, 1163, 1021 cm^{-1}; ^1H NMR (CD_3CN) δ 8.11 (d, J = 7.5 Hz, 4 H), 7.74 (t, J = 7.3 Hz, 2 H), 7.59 (t, J = 7.8 Hz, 4 H), 2.82 (s, 4 H); ^{19}F NMR (CD_3CN) δ −78.59 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 135.4, 133.8, 133.2, 117.0 (all Ph), 121.1 (q, J = 318 Hz, $CF_3SO_3^-$), 108.1 ($C{\equiv}CI^+$), 23.9 ($C{\equiv}CI^+$), 20.2 (CH_2); FAB HRMS m/z 632.869 331 ($M - CF_3SO_3^-$)$^+$, calcd for $C_{19}H_{14}F_3I_2O_3S$ 632.870 279. Anal. Calcd for $C_{20}H_{14}F_6I_2O_6S_2$: C, 30.69; H, 1.81. Found: C, 30.29; H, 1.80.

1,8-Bis[phenyl[(trifluoromethanesulfonyl)oxy]iodo]-1,7-octadiyne (9b). Reaction of 1,8-bis(tributylstannyl)-1,7-octadiyne (**5b**) (3.60 g, 5.27 mmol) with reagent **7** (4.10 g, 10.8 mmol) gave 4.00 g (93%) of **9b** as a white microcrystalline solid, mp 163–168 °C dec: IR (CCl_4) 3082, 2933, 2183 (C≡C), 1229, 1159, 1025 cm^{-1}; ^1H NMR (CD_3CN) δ 8.1 (d, J = 7.6 Hz, 4 H), 7.7 (t, J = 7.3 Hz, 2 H), 7.5 (t, J = 7.6 Hz, 4 H), 2.5 (t, J = 6.6 Hz, 4 H), 1.5 (t, J = 6.6 Hz, 4 H); ^{19}F NMR (CD_3CN) δ −78.65 (s, CF3SO$_3^-$); ^{13}C NMR (CD_3CN) δ 135.4, 133.8, 133.2, 117.0 (all Ph), 121.4 (q, J = 318 Hz, $CF_3SO_3^-$), 111.1 ($C{\equiv}CI^+$), 27.1 (CH_2), 21.8 ($C{\equiv}CI^+$), 20.35 (CH_2); FAB HRMS m/z 660.899 94 ($M - CF_3SO_3^-$)$^+$, calcd for $C_{21}H_{18}F_3I_2O_3S$ 660.901 66. Anal. Calcd for $C_{22}H_{18}F_6I_2O_6S_2$: C, 32.58; H, 2.24. Found: C, 32.63; H, 2.28.

1,9-Bis[phenyl[(trifluoromethanesulfonyl)oxy]iodo]-1,8-nonadiyne (9c). Reaction of 1,9-bis(tributylstannyl)-1,8-hexadiyne (**5c**) (3.69 g, 5.29 mmol) with reagent **7** (4.0 g, 10.6 mmol) gave 3.92 g (90%) of **9c** as a white microcrystalline solid, mp 134–136 °C dec: IR (CCl_4) 3080, 2951, 2187 (C≡C), 1291, 1216, 1162, 1025 cm^{-1}; ^1H NMR (CD_3CN) δ 8.12 (d, J = 7.6 Hz, 4 H), 7.74 (t, J = 7.3 Hz, 2 H), 7.60 (t, J = 7.8 Hz, 4 H), 2.56 (t, J = 6.8 Hz, 4 H), 1.40 (dt, J = 6.8 Hz, 4 H), 1.37 (m, 2 H): ^{19}F NMR (CD_3CN) δ −78.65 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 135.4, 133.7, 133.1, 117.0 (all Ph), 121.3 (q, J = 318 Hz, $CF_3SO_3^-$), 111.5 ($C{\equiv}CI^+$), 28.1 (CH_2), 27.5 (CH_2), 21.6 ($C{\equiv}CI^+$), 20.7 (CH_2); FAB HRMS m/z 674.916 54 ($M - CF_3SO_3^-$)$^+$, calcd for $C_{22}H_{20}F_3I_2O_3S$ 674.917 31.

Bis[phenyl[(trifluoromethanesulfonyl)oxy]iodo] Bis(propargyl) Ether (10). Reaction of bis(tributylstannyl) bis(propargyl) ether (**6**) (0.67 g, 1.0 mmol) with reagent **7** (0.75 g, 2.0 mmol) resulted in precipitation of compound **10** as an unstable oil, yield 0.62 g (78%): IR (neat) 3085, 3063, 2973, 2188 (C≡C), 1563, 1261, 1233, 1171, 1024 cm^{-1}; ^1H NMR (CD_3CN) δ 8.16 (d, J = 7.8 Hz, 4 H), 7.7 (t, J = 7.6 Hz, 2 H), 7.5 (t, J = 8.0 Hz, 4 H), 4.5 (s, 4 H); ^{19}F NMR (CD_3CN) δ −78.54 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 135.9, 134.2, 133.5, 117.2 (all Ph), 120.9 (q, J = 319 Hz, $CF_3SO_3^-$), 104.0 ($C{\equiv}CI^+$), 58.9 (CH_2), 31.6 ($C{\equiv}CI^+$); FAB HRMS m/z 648.863 298 ($M - CF_3SO_3^-$)$^+$, calcd for $C_{19}H_{14}F_3I_2O_4S$ 648.865 794.

General Procedure for the Reaction of Bis(phenyliodonium) Diyne Triflates with Triphenylphosphine. Triphenylphosphine (2 mmol) was added to a stirred suspension of the corresponding iodonium salt **8–10** (1 mmol) in CH_2Cl_2 (20 mL) at −78 °C under nitrogen. The mixture was allowed to warm to room temperature and stirred for 0.5 h, and then the solvent was removed by evaporation and the residue (an oil or a solid) washed with ether (50 mL) and dried in vacuo. Isolated solids could then be recrystallized from CH_2Cl_2 and ether.

1,4-Bis[[triphenyl[(trifluoromethanesulfonyl)oxy]phosphoranyl]ethynyl]benzene (11a). Reaction of **8a** (0.30 g, 0.36 mmol) with Ph_3P (0.19 g, 0.73 mmol) gave 0.32 g (94%) of **11a** as a yellow solid, mp >250 °C dec: IR (CCl_4) 3087, 3065, 3043, 2171 (C≡C), 1226, 1187, 1017 cm^{-1}; ^1H NMR (CD_3CN) δ 8.04 (m, 4 H), 7.9–7.6 (m, 30 H); ^{19}F NMR (CD_3CN) δ −78.04 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 137.04, 134.67 (d, J_{C-P} = 12.7 Hz), 131.60 (d, J_{C-P} = 13.9 Hz), 122.54 (d, J_{C-P} = 4.4 Hz) (all Ar), 122.12 (q, J = 321.9 Hz, $CF_3SO_3^-$), 118.98 (d, J_{C-P} = 100.4 Hz, ipso), 116.5 (d, J_{C-P} = 30.5 Hz, $C{\equiv}CP^+$), 73.40 (d, J_{C-P} = 184.2 Hz, $C{\equiv}CP^+$); ^{31}P NMR (CD_3CN) δ 8.22 (s, Ph_3P^+); FAB HRMS m/z 797.167 20 ($M - CF_3SO_3^-$)$^+$, calcd for $C_{47}H_{34}F_3O_3P_2S$ 797.165 59.

4,4′-Bis[[triphenyl[(trifluoromethanesulfonyl)oxy]phosphoranyl]ethynyl]biphenyl (11b). Reaction of **8b** (0.070 g, 0.077 mmol) with Ph_3P (0.040 g, 0.15 mmol) gave 0.06 g (76%) of **11b** as a yellow oil: IR (CCl_4) 3060, 2172 (C≡C), 1261, 1224, 1156, 1030 cm^{-1}; ^1H NMR (CD_3CN) δ 7.9–7.6 (m); ^{19}F NMR (CD_3CN) δ −78.69 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 144.18, 136.78 (d, J_{C-P} = 3.0 Hz), 135.58, 135.06 (d, J_{C-P} = 1.9 Hz), 134.45 (d, J_{C-P} = 12.3 Hz), 131.41 (d, J_{C-P} = 14.2 Hz), 128.78, (all Ar), 122.11 (q, J = 321.9 Hz, $CF_3SO_3^-$), 118.91 (d, J_{C-P} = 100.3 Hz, ipso) 117.73 (d, J_{C-P} = 30.1 Hz, $C{\equiv}CP^+$), 71.04 (d, J_{C-P} = 187.1 Hz, $C{\equiv}CP^+$); ^{31}P NMR (CD_3CN) δ 8.09 (s, Ph_3P^+); FAB HRMS m/z 873.196 171 ($M - CF_3SO_3^-$)$^+$, calcd for $C_{53}H_{38}F_3O_3P_2S$ 873.196 905.

1,6-Bis[triphenyl[(trifluoromethanesulfonyl)oxy]phosphoranyl]-1,5-hexadiyne (12a). Reaction of **9a** (0.30 g, 0.38 mmol) with Ph_3P (0.20 g, 0.76 mmol) gave 0.238 g (70%) of **11b** as a yellow oil: IR (CCl_4) 3063, 2959, 2929, 2205 (C≡C), 1223, 1151, 1059, 1029 cm^{-1}; ^1H NMR (CD_3CN) δ 7.9–7.6 (m, 30 H), 3.28 (d, J_{P-H} = 1.8 Hz, 4 H); ^{19}F NMR (CD_3CN) δ −78.04 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 136.84, 134.27 (d, J_{C-P} = 12.4 Hz), 131.47 (d, J_{C-P} = 14.1 Hz) (all Ph), 122.00 (d, J_{C-P} = 31 Hz, $C{\equiv}CP^+$), 122.1 (q, J = 322 Hz, $CF_3SO_3^-$), 119.18 (d, J_{C-P} = 100.3 Hz, ipso), 63.57 (d, J_{C-P} = 186.8 Hz, $C{\equiv}CP^+$), 19.84 (CH_2); ^{31}P NMR (CD_3CN) δ 6.82 (s, Ph_3P^+); FAB HRMS m/z 749.265 968 ($M - CF_3SO_3^-$)$^+$, calcd for $C_{43}H_{34}F_3O_3P_2S$ 749.265 604.

1,8-Bis[triphenyl[(trifluoromethanesulfonyl)oxy]phosphoranyl]-1,7-octadiyne (12b). Reaction of **9b** (0.41 g, 0.51 mmol) with Ph_3P (0.28 g, 1.10 mmol) gave 0.316 g (67%) of **11b** as a cream yellow microcrystalline solid, mp 165–167 °C dec: IR (CCl_4) 3087, 3063, 2958, 2198 (C≡C), 1223, 1188, 1077, 1029 cm^{-1}; ^1H NMR (CD_3CN) δ 7.9–7.6 (m, 30 H), 2.86 (m, 4 H), 1.9 (m, 4

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H); ^{19}F NMR (CD_3CN) δ −78.61 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 136.35, 133.28 (d, J_{C-P} = 12.8 Hz), 131.13 (d, J_{C-P} = 13.7 Hz) (all Ph), 125.20 (d, J_{C-P} = 31.2 Hz, C≡CP$^+$), 121.82 (q, J = 320 Hz, $CF_3SO_3^-$), 119.4 (d, J_{C-P} = 100.1 Hz, ipso), 61.97 (d, J_{C-P} = 189.6 Hz, C≡CP$^+$), 26.77 (CH_2), 20.63 (d, J_{C-P} = 3.8 Hz, CH_2); ^{31}P NMR (CD_3CN) δ 6.80 (s, Ph_3P^+); FAB HRMS m/z 777.197 02 (M − $CF_3SO_3^-$)$^+$, calcd for $C_{45}H_{38}F_3O_3P_2S$ 777.196 89.

1,9-Bis[triphenyl[(trifluoromethanesulfonyl)oxy]-phosphoranyl]-1,8-nonadiyne (12c). Reaction of **9c** (0.20 g, 0.24 mmol) with Ph_3P (0.13 g, 0.50 mmol) gave 0.176 g (78%) of **12c** as a yellow oil: IR (CCl_4) 3084, 3064, 2935, 2202 (C≡C), 1224, 1188, 1031 cm^{-1}; ^{1}H NMR (CD_3CN) δ 7.9–7.6 (m, 30 H), 2.77 (m, 4 H), 1.80 (m, 4 H), 1.59 (m, 2 H); ^{19}F NMR (CD_3CN) δ −78.65 (s, $CF_3SO_3^-$); ^{13}C NMR (CD_3CN) δ 136.39 (d, J_{C-P} = 2.8 Hz), 134.01 (d, J_{C-P} = 12.8 Hz), 131.13 (d, J_{C-P} = 13.9 Hz) (all Ph), 125.68 (d, J_{C-P} = 31.0 Hz, C≡CP$^+$), 121.8 (q, J = 320 Hz, $CF_3SO_3^-$), 119.49 (d, J_{C-P} = 100.6 Hz, ipso), 61.77 (d, J_{C-P} = 190.5 Hz, C≡CP$^+$), 28.77 (CH_2), 26.91 (CH_2), 20.99 (d, J_{C-P} = 3.5 Hz, CH_2); ^{31}P NMR (CD_3CN) δ 6.69 (s, Ph_3P^+); FAB HRMS m/z 791.212 45 (M − $CF_3SO_3^-$)$^+$, calcd for $C_{46}H_{40}F_3O_3P_2S$ 791.212 54.

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Registry No. **4a**, 122482-73-9; **4b**, 138877-31-3; **5a**, 138877-32-4; **5b**, 138877-33-5; **5c**, 138877-34-6; **6**, 138877-35-7; **7**, 138877-36-8; **8a**, 138877-37-9; **8b**, 138877-39-1; **9a**, 138877-41-5; **9b**, 138877-43-7; **9c**, 138877-45-9; **10**, 138877-47-1; **11a**, 138877-49-3; **11b**, 138877-51-7; **12a**, 138877-53-9; **12b**, 138877-55-1; **12c**, 138877-57-3; Ph_3P, 603-35-0.

Supplementary Material Available: ^{1}H and ^{13}C NMR spectra of all compounds for which elemental analyses were not obtained (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

Stereoselective Synthesis of β-Lactams by Oxidative Coupling of Dianions of Acyclic Tertiary Amides†

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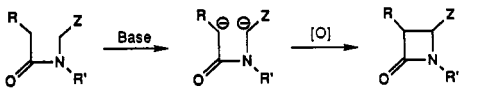
Tertiary amides $RCH_2CON(R')CH_2Z$, where Z is an electron-withdrawing group, were converted into dianions by treatment with 2 equiv of *n*-butyllithium or *tert*-butyllithium, and the dianions were oxidized with *N*-iodosuccinimide (NIS) or a Cu(II) carboxylate to form β-lactams stereoselectively. The stereochemistry of β-lactam formation depends on the oxidant; NIS is cis-selective, whereas Cu(II) is nonselective or slightly trans-selective. A high degree of asymmetric induction in the formation of β-lactams was achieved by using (*R*)-1-phenylethylamine as a chiral auxiliary. This asymmetric ring closure was applied to the preparation of *cis*-β-lactam **31**, an intermediate for the synthesis of the monobactam antibiotic carumonam.

Introduction

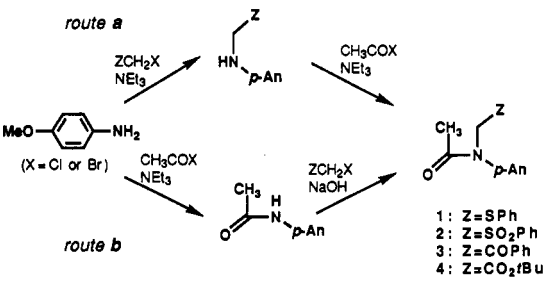
During the last few decades, numerous publications have appeared on the synthesis of β-lactams.[1] The reactions employed for forming the azetidinone ring can be roughly classified as follows:[2] (i) ketene–imine [2 + 2] cycloaddition, (ii) olefin–isocyanate [2 + 2] cycloaddition, (iii) aldol-type reactions of an ester enolate with an imine, (iv) intramolecular condensation of a β-amino acid, (v) intramolecular substitution of a β-hetero-substituted amide, and (vi) cyclization of an α,β-epoxy amide. All these methods involve *substrate control*; i.e., the stereochemistry of β-lactam formation is controlled by the structure of a precursor. Accordingly, β-lactams of undesired stereochemistry can be produced from some precursors.[3] We have been exploring a new method which allows us to control the stereochemistry of ring formation by proper choice of a reagent (*reagent control*). This paper details the synthesis of β-lactams through an intramolecular oxidative coupling of dianions generated from acyclic tertiary amides,[4] wherein the choice of oxidant is crucial for the control of stereochemistry.

The basic concept of the present reaction is summarized in Scheme I. An amide $RCH_2CON(R')CH_2Z$, wherein R and R′ are substituents or protecting groups and Z is an electron-withdrawing group, is converted into the corresponding dianion with 2 molar equiv of base. Intramolecular oxidative coupling of the dianion gives the desired

Scheme I



Scheme II



† Dedicated to Professor Hitosi Nozaki on the occasion of his 70th birthday.

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