(2 mL) was added and evaporated to remove residual H_2O. This process was repeated three times. The reaction flask was then filled with nitrogen and dry toluene (2 mL) to dissolve the initiator. ε-Caprolactone (2.89 g, 25.3 mmol) was added, and the temperature was increased to 110 °C before a catalytic amount of $Sn(Oct)_2$ was added. The catalyst/initiator ratio was 1/400. The polymerization mixture was stirred for 24 h, diluted with THF, and poured into cold MeOH to precipitate a white crystalline powder. Yield: 3.7 g (98 %). ^1H NMR ($CDCl_3$): $\delta = 1.30-1.42$ (m, poly; CH_2), 1.55–1.69 (m, poly; CH_2), 2.26–2.32 (t, poly; CH_2O), 3.60–3.65 (t, 18H; CH_2OH), 4.01–4.07 (t, poly; CH_2CO), 4.33 (s, 12H; $CCH_3(CH_2O)_2$), 6.88–7.24 (m, 12H; Ph); ^{13}C NMR ($CDCl_3$): $\delta = 17.74$, 24.50, 25.45, 28.27, 32.20, 34.03, 46.69, 51.58, 62.38, 64.05, 65.07, 120.67, 129.64, 146.22, 148.60, 171.37, 172.78, 173.65.

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A Novel Domino Reaction: Cyclization of Alkynyl Sulfides by Reaction with IPy_2BF_4[**]

José Barluenga,[*] Gustavo P. Romanelli, Lorenzo J. Alvarez-García, Isidro Llorente, José M. González, Esther García-Rodríguez, and Santiago García-Granda

Synthetic methodologies relying on transition metal chemistry have opened unusual approaches to polycyclic structures.[1, 2] Intramolecular cyclizations of diynes mediated by organometallic complexes[3] often take place according to an *exo-exo* coupling mode,[4] whereas *endo-endo*[3] and *exo-endo*[5, 6] cyclizations have rarely been observed (Figure 1). Described here is a novel approach to accomplish the *exo-endo* cyclization of α,ω-diynes, and preliminary studies on a related intermolecular process.

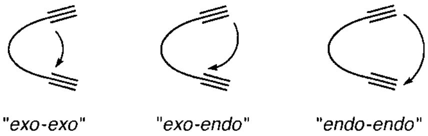

Figure 1. Possible intramolecular cyclizations. The arrow shows the carbon–carbon bond formed in the metal-promoted intramolecular cyclization as a function of the diyne coupling mode.

Bis(pyridyl)iodonium(I) tetrafluoroborate (IPy_2BF_4) can be efficiently used as a catalyst or a stoichiometric reagent for unconventional coupling reactions of 1-iodoalkynes[7] and 1-*t*BuMe$_2$Si-substituted alkynes.[8] These two processes were restricted to aryl-substituted alkynes. Now, we have found for the first time that upon activation by sulfur substituents aliphatic alkynes can enter in a carbocyclization process mediated by IPy_2BF_4. This provides a new entry to unusual *exo-endo* intramolecular cyclizations of α,ω-diynes, as depicted in Scheme 1 for the conversion of the acetylenic sulfide **1a**[9] derived from 1,6-heptadiyne.[10] The overall process comprises two different carbon–carbon bond forming reactions—namely, an alkyne–alkyne coupling and a novel Friedel–Crafts-like ring closure—and is thus a new domino reaction.[11] The process is very fast at low temperature and is completed within a few minutes; increasing the reaction time results in lower yields owing to significant side processes. The reaction takes place upon addition of the starting diynyl

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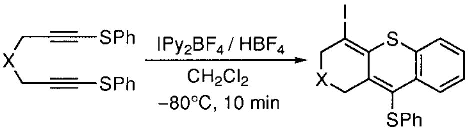


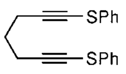
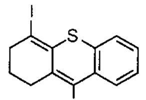
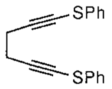
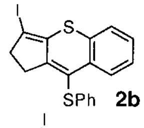
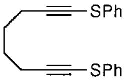
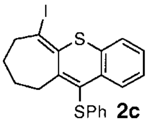
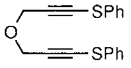
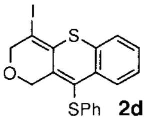
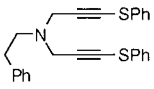
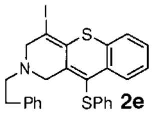
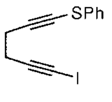
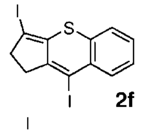
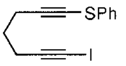
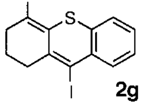
1a X: CH$_2$ (92%) **2a**
1d X: O (68%) **2d**

Scheme 1. Intramolecular cyclization of α,ω-diynyl sulfides **1** upon reaction with IPy$_2$BF$_4$/HBF$_4$.

sulfide **1** to a cooled solution of IPy$_2$BF$_4$ (0.1 M in CH$_2$Cl$_2$) and HBF$_4$ (the acid activates the iodonium salt to furnish the reactive species;[12] molar ratio IPy$_2$BF$_4$:HBF$_4$ = 1:1, larger amounts of acid give poorer yields).

The scope of the reaction is indicated in Table 1.[13] Reactions 1, 4, and 5 show that the process can be used to form three linearly condensed six-membered rings from the corresponding 1,6-diynes. Moreover, it is compatible with the presence of different heteroatoms in the alkyl tethering chain. Spectroscopic data of the products are in agreement with the proposed structure, which was firmly established by an X-ray analysis of **2d**.[14] The use of phenyl sulfides derived from 1,5-hexadiyne allows the synthesis of a polycyclic structure **2b** containing five- and six-membered rings in a very rapid reaction (about two minutes).

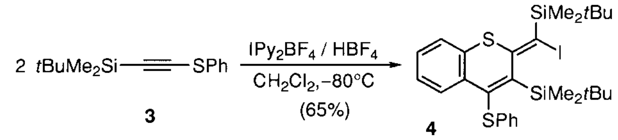
Table 1. Intramolecular *exo-endo* dimerization of α,ω-diynyl sulfides mediated by IPy$_2$BF$_4$.

Reaction	Substrate **1**	Product **2**	Yield [%][a]
1		 **2a**	92
2		 **2b**	69
3		 **2c**	71[b]
4		 **2d**	72
5		 **2e**	52
6		 **2f**	44
7		 **2g**	31

[a] Yield of isolated crystalline materials, based on the starting diyne. [b] Two equivalents of IPy$_2$BF$_4$/HBF$_4$ were used.

Interestingly, 1,7-diynes also react efficiently to furnish **2c**, a condensed structure featuring a medium-sized seven-membered ring, as proven by X-ray analysis.[14] This flexible synthesis of condensed thiin structures is efficient and starts from simple acyclic precursors. It takes advantage of the phenyl sulfide moiety to intramolecularly capture intermediate reactive species formed upon diyne dimerization. This step is very fast and, according to ^{1}H NMR spectroscopy, occurs even in the presence of external nucleophiles such as MeOH or *i*PrOH (as cosolvents) without addition of the alcohol to the reaction product. The activation of one triple bond by sulfur is essential for the first C–C bond forming step, but the second one might be replaced by a different substituent. Entries 6 and 7 show that mixed compounds substituted by sulfur and iodine cyclize in a related way, yielding interesting diiodinated structures. In contrast, no cyclization occurs with α,ω-diiododiynes.

We tested the reactivity of 1-hexynyl phenyl sulfide to explore a possible intermolecular coupling. Although the reaction proceeds in a similar way,[15] yields have so far been poor. Nevertheless, it shows that simple alkynes are compatible with this coupling. PhSC≡CSiMe$_2$*t*Bu (**3**) was a good model compound for the intermolecular coupling. Upon reaction of **3** with IPy$_2$BF$_4$/HBF$_4$ in CH$_2$Cl$_2$ (5×10^{-2} M) for 4 h, the temperature raised from −80 °C to 0 °C, and **4** was obtained (Scheme 2).[13, 14] The transformation of **3** to **4** also involves two different and sequential C–C bond forming reactions; the overall result is a regio- and stereoselective synthesis of a cyclic framework. The 1,3-diene moiety within the reaction product involves an interesting arrangement of five well-differentiated positions substituted with heteroatoms. Furthermore, the large torsional angle (74.1°) between the *exo*cyclic double bond and the C–Si bond (where C belongs to the cyclic frame) represents a remarkable structural motif, resulting in an unusual source of helical chirality.[16]



Scheme 2. Intermolecular coupling reaction of **3** upon reaction with IPy$_2$BF$_4$/HBF$_4$.

A tentative mechanism accommodating these results might involve an initial attack of the electrophilic iodine atom to a triple bond in **1c** to produce cation **A**,[17] a relatively stable vinyl cation substituted in the α position by sulfur (Scheme 3).[18, 19] Collapse of **A** by C–C bond formation would result in assembly of the first ring and creating of the new and reactive vinyl cation **B**.[20] The latter affords **2c** by subsequent ring closure involving participation of the phenyl group attached to sulfur.

A novel and synthetically valuable *exo-endo* intramolecular cyclization of α,ω-diynes has been developed, and the feasibility of the intermolecular coupling explored. An interesting feature is that the iodine promoting the reaction

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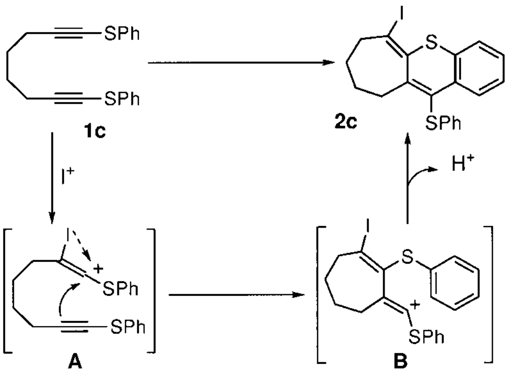
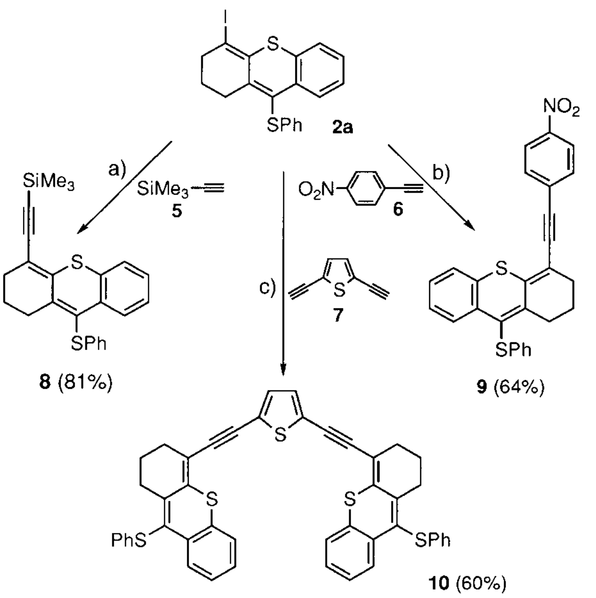


Scheme 3. Proposed mechanism for the intramolecular cyclization of **1c** into **2c**.

can be exploited for further elaboration of the polycyclic frame, as for instance depicted in Scheme 4.[21] This fact, and the electronic tuning of the reactivity of the triple bond by other substituents in this type of reaction, might open new and unconventional synthetic pathways.



Scheme 4. Some synthetic transformations of the newly formed C–I bond in **2a**. Conditions for all reactions: reagent **5**, **6**, or **7**; [$PdCl_2(PPh_3)_2$]/CuI (cat.); Et_3N/THF; room temperature; 5 h (a), 30 h (b), or 17 h (c).

Experimental Section

All reactions were carried out under a positive pressure of nitrogen. Dichloromethane was dried by refluxing over P_2O_5 and distilled under a nitrogen atmosphere.

Reaction of diynes with IPy_2BF_4: IPy_2BF_4 (3.72 g, 10.0 mmol, 1.0 equiv) was dissolved in dry CH_2Cl_2 (100 mL) and stirred for 5 min. The solution was cooled to $-80\,^{\circ}C$, and tetrafluoroboric acid (1.36 mL, 54% solution in diethyl ether, 10.0 mmol, 1.0 equiv) was added by syringe. After 10 min a solution of the diyne (10.0 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) was added, and the reaction mixture was stirred. The reaction was quenched with a 10% aqueous solution of $Na_2S_2O_3$ (100 mL). The organic layer was washed with water (2 × 100 mL), dried over sodium sulfate, and concentrated. The products were purified by filtration through a short column of neutral aluminum oxide with hexane/ethyl acetate as eluent and recrystallization from mixtures of hexane and diethyl ether.

2a: Yellow solid, m.p. 102–103 °C; UV/Vis (CH_3OH): λ_{max} (ε) = 203 (40000), 263 (37500), 385 (8000), 484 nm (5500); IR (KBr): $\tilde{\nu}$ = 3057, 3052, 2996, 2976, 2953, 2928, 2907, 1580, 1535, 1470, 1437, 1427, 754, 743, 725, 689 cm^{-1}; ^1H NMR ($CDCl_3$): δ = 7.91 (d, J = 8.1 Hz, 1 H), 6.95–7.30 (m, 8 H), 3.12 (t, J = 6.0 Hz, 2 H), 2.91 (t, J = 6.0 Hz, 2 H), 1.84 (quint, J = 6.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$): δ = 141.1 (s), 136.4 (s), 133.0 (s), 132.0 (s), 130.4 (s), 129.0 (d), 128.6 (d), 127.7 (d), 125.9 (s), 125.8 (d), 125.6 (d), 125.0 (d), 124.4 (d), 98.0 (s), 42.4 (t), 31.0 (t), 24.2 (t); HR-MS (EI) calcd for $C_{19}H_{15}IS_2$: 433.9653; found: 433.9659; elemental analysis calcd for $C_{19}H_{15}IS_2$: C 52.54, H 3.48; found: C 52.65, H 3.53.

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[13] All compounds **2** reported in Table 1 were fully characterized, and their spectroscopic and analytical data firmly support the proposed structures. For reaction conditions, a full list of ^{13}C and ^1H NMR data, representative UV/Vis, IR, and MS data and elemental analyses, see the supporting information.

[14] The structures of **2c**, **2d**, and **4** were determined by X-ray analysis. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102304 (**4**), CCDC-102305 (**2c**), and CCDC-102306 (**2d**). Copies of the data can be obtained free of charge on application to

CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail:deposit@ccdc.cam.ac.uk).

[15] Selected data for the dimer: HR-MS (EI) calcd for $C_{24}H_{27}IS_2$: 506.0599; found: 506.0603; ^{13}C NMR ($CDCl_3$): $\delta = 95.8$ (CI).

[16] Review: K. P. Meurer, F. Vögtle, *Top. Curr. Chem.* **1985**, *127*, 1–76; see also: A. Beck, R. Gompper, K. Polborn, H.-U. Wagner, *Angew. Chem.* **1993**, *105*, 1424–1427; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1352–1354; B. L. Feringa, N. P. M. Huck, A. M. Schoevaars, *Adv. Mater.* **1996**, *8*, 681–684.

[17] For addition reactions to alkynyl sulfides promoted by IPy_2BF_4, see J. Barluenga, P. J. Campos, F. López, I. Llorente, M. A. Rodríguez, *Tetrahedron Lett.* **1990**, *31*, 7375–7378.

[18] For the directive effect of sulfur on electrophilic addition to acetylene, see G. Modena, U. Tonellato, *Adv. Phys. Org. Chem.* **1971**, *9*, 185.

[19] Alternative radical pathways cannot be ruled out, but should occur in an *exo-exo* mode (according to S. Caddick, C. L. Shering, S. N. Wadman, *Chem. Commun.* **1997**, 171–172). No evidence for significant sulfur oxidation was found during the reaction. Moreover, the addition of BHT to the reaction mixture did not affect the cyclization.

[20] M. Hanack, *Angew. Chem.* **1978**, *90*, 346–354; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 333–341.

[21] Compound **9** and related structures based on alkene linkers could be of interest for second-order nonlinear optics: S. R. Marder, J. W. Perry, *Adv. Mater.* **1993**, *5*, 804–815; M. S. Wong, C. Bosshard, F. Pan, P. Günter, *Adv. Mater.* **1996**, *8*, 677–680; M. S. Wong, C. Bosshard, P. Günter, *Adv. Mater.* **1997**, *9*, 837–842. Furthermore, **10**, or related compounds from the coupling of **7** with diiodides **2f** or **2g**, could be precursors for new poly(aryleneethynylene) (PAE) polymers containing 2,5-thienylene units: T. Yamamoto, K. Honda, N. Ooba, S. Tomaru, *Macromolecules* **1998**, *31*, 7–14.

Polycephalin B and C: Unusual Tetramic Acids from Plasmodia of the Slime Mold *Physarum polycephalum* (Myxomycetes)**

Alexander Nowak and Bert Steffan*

Light plays an important role during the life cycle of the myxomycete *Physarum polycephalum*.[1] Young plasmodia, which are of a remarkable yellow color, live inside decaying trees and move away from the light, while older plasmodia, which have stopped growing, move towards the light and sporulate. Photoreceptors in the UV-A or blue light range which contain maxima at 350 nm (UV-A) and 460 nm (blue light) in their action spectra are responsible[1b] for these phenomena.

Despite intensive efforts the nature of the photoreceptor concerning this "blue-light phenomenon" is as yet unknown. Different types of pigments such as pteridines,[2] phenols,[3] peptides, flavines, flavones, nitrogen-containing polyenes,[4] or phytochromes[5] were assumed to be involved in the signal cascade. Since not only the yellow plasmodia of wild-type *P. polycephalum* but also the white mutants are photosensitive, it was considered that the chromophore of the blue-light receptor may be a flavin or a pteridine and that the orange-yellow pigments occuring in the wild type have no function for the signal transduction.

We were able to prove that the yellow wild type as well as the white mutant LU 897 × LU 898[6] contain a very similar but only quantitatively different set of pigments of the polyene type absorbing in the range under consideration.[7] Taking into account that the UV maximum of a chromophore can be bathochromically shifted up to 80 nm by integration into a protein, as described for the photoreceptor of the halophilic purple bacterium *Ectothiorhodospira halophila*,[8] the yellow polyenes in *Physarum* plasmodia can be thought of as acting as antenna pigments within a protein or protein complex of this organism.

High-performance liquid chromatography (HPLC) of a myxomycete culture exposed to diffuse light after growing for five days under exclusion of light shows remarkable differences in the intensities of certain peaks in comparison to a myxomycete culture growing under exclusion of light only (Figure 1).[9] Apparently light stimulates the formation of two metabolites, which cause a striking increase in the intensities of peak 1 ($t_{ret} = 34.47$ min) and peak 2 ($t_{ret} = 32.74$ min). Here we report on the isolation and structure elucidation of these metabolites, which we have named polycephalin C (**1**) and B (**2**).

Because the compounds are very sensitive to light, all steps from incubation and extraction to chromatography were carried out under exclusion of light and at low temperature (4 °C). Plasmodia cultivated under axenic conditions[10] were first thoroughly extracted with a mixture of acetone, meth-

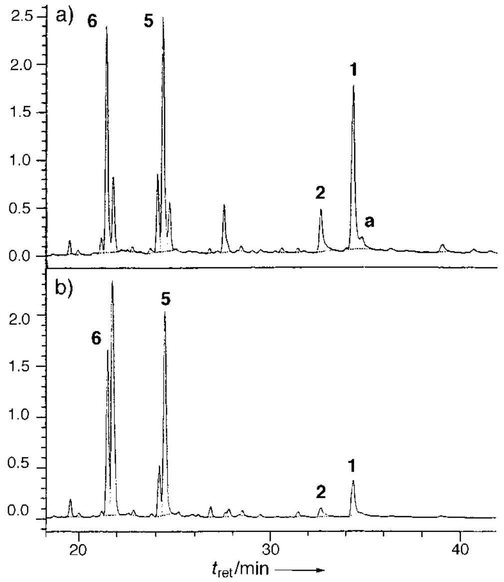

Figure 1. HPLD chromatograms for the chloroform extract of *P. polycephalum* cultures: a) growth for five days in the dark followed by two days under illumination; b) growth for seven days in the dark (control). Conditions for HPLC: column: Nucleosil 100–5 C_{18} (250 × 4 mm), mobile phase A: water/acetonitrile (9/1), 0.1 % TFA, mobile phase B: acetonitrile, 0.1 % TFA, linear gradient from A to B in 45 min, flow rate: 1.0 mL min^{-1}, photodiode array detection in the range of $\lambda = 200–800$ nm. A = absorbance, t_{ret} = retention time, TFA = trifluoroacetic acid.

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