Reactions of (*tert*-Butyldimethylsilyl)alkynes with IPy_2BF_4: Selective Synthesis of Novel Head-to-Head Dimers

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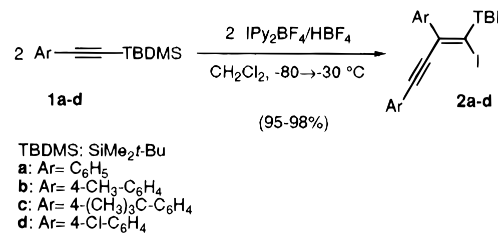
The straightforward elaboration of enynes by transition-metal-mediated linear dimerization of terminal alkynes is, in many cases, of limited synthetic value, mainly due to the formation of dimers as mixtures of regio- and stereoisomers with products arising from competitive further oligomerization reactions.[1] Thus, although remarkable examples of successful preparation of enynes using this approach had been reported,[2] alternative sp^2−sp coupling reactions are commonly the choice to assemble this organic frame.[3] The considerable current interest in acetylene chemistry,[4] recent efforts focusing on selective dimerization of alkynes,[5] and our finding of IPy_2BF_4-catalyzed head-to-tail dimerization of iodoalkynes[6] prompted us to explore the reactivity of (trialkylsilyl)alkynes toward this reagent that, eventually, might led to highly functionalized enynes through a new "C−C" bond-forming reaction.[7] Herein, we report an unprecedented coupling of (trialkylsilyl)acetylenes **1** upon reaction with IPy_2BF_4/HBF_4[8] (Py = pyridine) furnishing the regio- and diastereoisomerically pure enynes **2**. Moreover, at higher temperature, the enynes **2** further react with IPy_2BF_4 affording enynes **4** in another selective and efficient process.

Alkynylsilanes easily give substitution products upon reaction with simple electrophiles,[9] nevertheless, the reactivity of the "Si−C(sp)" σ-bond can be strongly modulated by the remainder substituents onto silicon.[10] TMS-protected terminal acetylenes (TMS = Me_3Si) led only to iodoalkynes upon reaction with IPy_2BF_4/HBF_4; however, at low temperature, TBDMS-alkynes **1** (TBDMS = *t*-$BuMe_2Si$) react with IPy_2BF_4 furnishing 2,4-diaryl-1-iodo-1-(*tert*-butyldimethylsilyl)-1,3-enynes **2**, resulting in a new and selective method for the homocoupling of alkynylsilanes[11] (eq 1).

Table 1. Dimers **2** and **4**[a]

starting material	product	*T* (h)	yield (%)[b]	starting material	product	*T* (h)	yield (%)[b]
1a	**2a**	20	95	**2c**	**4c**	5	95
1b	**2b**	5	99	**2d**	**4d**	16	90
1c	**2c**	5	99	**1a**	**4a**	24	95
1d	**2d**	16	97[c]	**1b**	**4b**	14	98
2a	**4a**	10	93	**1c**	**4c**	14	97
2b	**4b**	5	98	**1d**	**4d**	50	85[c]

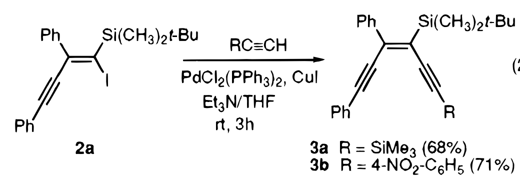
[a] See eqs 1 and 3. [b] Isolated yield. [c] Excess of IPy_2BF_4/HBF_4 was used (1:2 molar ratio to the starting material).



(1)

Head-to-tail dimers **2** were clean and efficiently obtained by mixing a 1:1:1 molar ratio of **1** to IPy_2BF_4 and HBF_4 (**1d** required 1:2 molar ratio of IPy_2BF_4/HBF_4) in CH_2Cl_2[12] and stirring the mixture for several hours (Table 1) at −80 to −30 °C (0 °C for **2a** and **2d**), followed by aqueous workup. Related aliphatic alkynylsilanes failed to couple under the same conditions. The proposed structure for **2** relies on spectroscopic (1D, 2D, and NOE NMR experiments) and analytical data.[13]

The above described homocoupling of alkynylsilanes yields enynes **2** functionalized in a way that makes them valuable for further synthetic transformations. Thus, for instance, it enables a short elaboration of enediyne cores from alkynes,[14] as depicted for the synthesis of **3**[15] (eq 2).



(2)

The rich chemistry of the I−C(sp^2) bond adds synthetic potential to this coupling reaction and clearly establishes a significant difference with respect to methods relying upon transition-metal-catalyzed reaction of terminal alkynes, where a new C−H rather than a C−I bond is formed in the final product.

Moreover, dimers **2** were also unexpected starting materials for a new and selective process giving (*E*)-1,4-diaryl-1,2-diiodo-1,3-butadiynes **4** (eq 3). Pure samples of compounds **2** react

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(15) X-ray analysis of **3b** proves its structure and, furthermore, confirms the proposed regio- and stereochemistry for the reaction of alkynylsilanes yielding the homocoupled compounds **2**. For crystal data of **3b** and a figure, see the Supporting Information.

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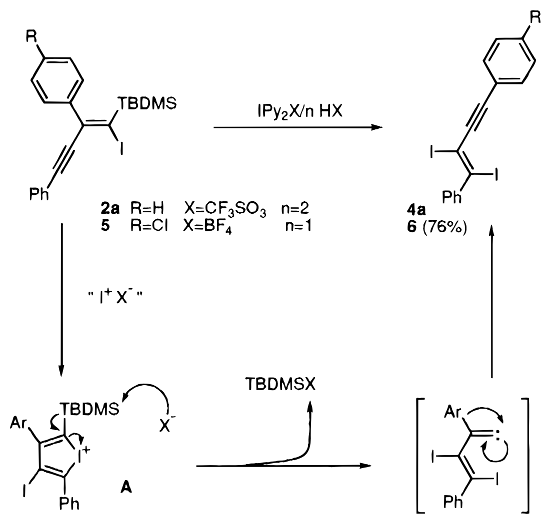
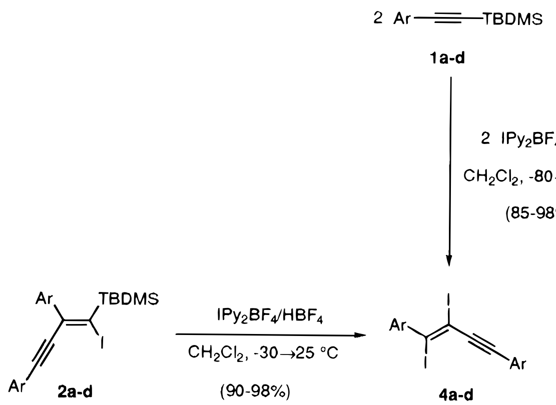
Scheme 1. Proposed Mechanism



(1:1 molar ratio) with IPy_2BF_4/HBF_4 affording enynes **4**, in excellent yield (Table 1, at −30 °C to room temperature, IPy_2BF_4 2.5 × 10^{-2} M in CH_2Cl_2). Interestingly, compounds **4** can



(3)

also be prepared from the readily available alkynes **1**,[16] using a 1:1:1 molar ratio of **1** to IPy_2BF_4 and HBF_4 (IPy_2BF_4/HBF_4 = 1:2, for **1d**), where the reaction time (see Table 1) and temperature (from −80 to 0 °C for **4b**,**c**, and to room temperature for **4a**,**d**) represent the differences in the experimental conditions with respect to those furnishing dimers **2**. Spectroscopic and analytical data support the proposed structure for dimers **4**, which was confirmed by an X-ray analysis of **4c**.[17]

To gain further insights into the conversion of enynes **2** to **4**, the cross-coupled dimer **5** was prepared by linear dimerization of the parent-substituted alkynes using IPy_2BF_4.[18] Upon reaction with IPy_2BF_4/HBF_4 (1:1 molar ratio to **5**) from 0 °C to room temperature for 16 h, only the enyne **6** was obtained, in 76% isolated yield, as depicted in Scheme 1. The reaction pathway includes several steps, namely, removal of the TBDMS group, migration of the aryl group labeled with chlorine from an internal to a terminal position, and migration of the already present iodine atom together with incorporation of an additional one. This transformation, resulting in the formation of three new σ-bonds and altering two π-bonds in the frame, is remarkably selective. A tentative mechanistic interpretation accounting for the conversion of dimers **2** into **4** is outlined in Scheme 1.

(16) Both 1,1-diiodo-2,4-disubstituted 1,3-butenynes (ref 6) and (*E*)-1,2-diiodo-1,4-disubstituted 1,3-butenynes can be selectively prepared upon reaction of the alkyne with IPy_2BF_4, simply by prior substitution at the terminal position by iodine or TBDMS, respectively.

(17) For crystal data of **4c**, including interesting -C−I···π and -C−H···π bonding interactions and a figure, see the Supporting Information.

(18) Prepared in an unoptimized 35% isolated yield, adapting the synthesis above described for **2**, starting from **1d** and PhC≡CI (2:1 molar ratio, respectively), at −60 °C for 40 h, and 2:1 molar ratio of HBF_4 to IPy_2BF_4.

Initial steps might comprise chemoselective attack of electrophilic iodine to the triple bond,[19] followed by five-membered ring closure involving 1,4-neighboring iodine participation[20,21] giving an iodolium ion[22] which has been detected by low-temperature NMR experiments.[23] ^1H and ^{13}C NMR spectra at −30 °C of the crude material obtained by reaction of **2a** with 1.0 equiv of $IPy_2CF_3SO_3$ and 2.0 equiv of CF_3SO_3H in $CDCl_3$ showed a silylated intermediate that underwent rearrangement to the head-to-head dimer **4a** upon warming up to room temperature, whose NMR data are consistent with the cyclic iodolium ion **A** shown in Scheme 1 (Ar = Ph, X = CF_3SO_3). The assignment of the signals was based on 2D NMR heteronuclear and NOE difference experiments. Deshielding in the ^{13}C NMR spectrum of the Si,I-bearing carbon atom (from 118.0 ppm in **2a** to 144.5 ppm), the pair of acetylenic carbons (from 96.3 and 97.6 to 108.1 and 134.5 ppm for the C−I and C−I^+, respectively), and the vinylic carbon bearing the aryl group (Ar = Ph, from 144.9 to 168.0 ppm) was observed and supports the existence of the cyclic iodolium ion.[24] A reasonable path for the evolution of this intermediate could involve counterion attack onto silicon[25] with concomitant loss of iodine that would migrate in a 1,4-sense affording an alkylidenecarbene,[26] from which a 1,2-aryl rearrangement furnishing an alkyne is also well-documented in hypervalent iodonium chemistry.[27]

In short, head-to-tail dimers **2** and head-to-head dimers **4** can be prepared from acetylenes **1** upon reaction with IPy_2BF_4. This manifold has not been reported in related coupling of alkynes mediated by transition metals. Other worthy features of this transformation include the yields and the noted regio- and stereoselectivity. The reactivity of the C−I bond formed in the reaction should enlarge the synthetic utility of this homocoupling process. Further work on the use of IPy_2BF_4 as a reagent simulating the outcome of transition-metal-based reactions of alkynes is in progress.

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Supporting Information Available: Characterization data for **2**−**7** and **A**, X-ray figures, and relevant features for **3b** and **4c**, NMR spectra for **A**, and X-ray crystallographic data for compounds **3b** and **4c** including tables of atomic coordinates, bond lengths and bond angles (40 pages). See any current masthead page for ordering and Internet access instructions.

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(25) The unique combination of silicon and positive iodine in one carbon and a mild source of F^- toward silicon provides a driving force to the formation of **4**. Related 2,4-diphenyl-1,1-diiodo-1,3-butenyne does not undergo this reaction, giving (*E*)-1,1,3,4-tetraiodo-2,4-diphenyl-1,3-butadiene **7**.

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