Triisopropylsilyl Protected Hexa-1,5-diyne-3,4-dione: A Convenient Precursor to 2,3-Dialkynyl 1,4-Diazabutadienes

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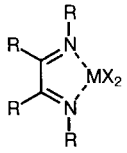
Abstract: Diazabutadienes with a 2,3-dialkynyl substitution pattern are easily accessible by reaction of silyl-protected dialkynyl-1,2-diones with primary aromatic amines.

The development of diimine-ligated transition metal complexes **1** as components of efficient catalyst systems for olefin polymerisation by Brookhart *et al*.[1] has inspired a renewed interest in the chemistry of 1,4-diazabuta-1,3-dienes. The steric and the electronic properties of these versatile ligands[2] can be fine-tuned by varying the substituents at the nitrogens and/or at the internal carbon centers of the diazabutadiene backbone.



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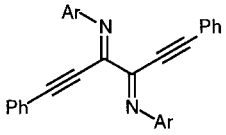
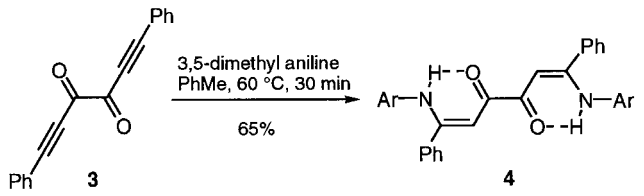


2

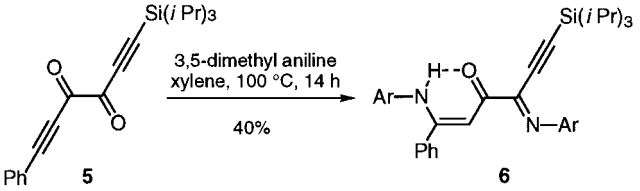
Previously, substitution at the 2,3 positions was limited to H, Me or aryl until we recently reported a general route for the introduction of organyl groups by a palladium-mediated cross-coupling procedure starting from bis(imidoyl chlorides) and organostannanes.[3] A particularly intriguing result of this work was the successful preparation of the first 2,3-dialkynyl 1,4-diazabutadienes as exemplified by **2**. Our interest in small acetylenic building blocks for the assembly of alkynylated near-infrared chromophores fueled continuous efforts to explore synthetic methods for their generation. Reported below is an alternative route for the preparation of dialkynyl diazabutadienes starting from a bis(triisopropysilyl)-protected dialkynyl 1,2-dione.[4,5]

Initial attempts to generate dialkynyl diazabutadienes by simply condensing 1,6-diphenylhexa-1,5-diyne-3,4-dione **3**[4,5] with primary aromatic amines were hampered by the dominant 1,4-addition to the reactive ynone-moiety. Hence, treatment of **3** with 3,5-dimethylaniline in toluene furnished exclusively the vinylogous bisamide **4**, whose double bond geometry was ascertained by NMR spectroscopy. While this mode of addition to the dialkynyl diones points the way to a convenient entry into bi-heterocyclic structures and β-amino acids, it obviously obstructs the formation of diazabutadiene derivatives.



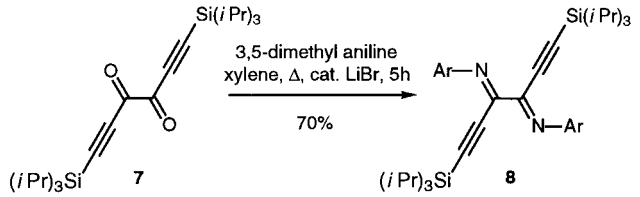
3 **4**

Our earlier work on dialkynyl diketones[4,5] had reconfirmed the fact that the bulky triisopropylsilyl group may serve as an efficient control element by sterically shielding the alkyne unit to which it is attached.[6] We therefore treated triisopropysilyl protected dialkynyl-1,2-diones with aniline derivatives, hoping that the terminal substituent would direct the nucleophilic attack of the amine nitrogen to the ketone moiety. Indeed, the unsymmetrically substituted diketone **5**,[4] bearing one terminal phenyl- and one triisopropylsilyl-substituent, gave 1,4- as well as 1,2 addition in xylene to furnish **6**.



5 **6**

Consequently, and most gratifyingly, shielding both alkyne units of the diketones by triisopropylsilyl groups as in **7**[5] led to the targeted dialkynyl diazabutadiene in 70% yield after reaction with two equiv. 3,5-dimethyl aniline in refluxing xylene in the presence of catalytic amounts of LiBr.[7]



7 **8**

It is evident from these findings that the preparation of acetylenic diazabutadienes by this procedure is limited to precursors with sterically encumbered alkynyl groups. Since terminal alkynes bearing a less bulky substituent are readily introduced by palladium-mediated cross-coupling procedures from bis(imidoyl chlorides),[3] the above diimine formation from **7** represents a useful complementary entry to dialkynyl diazabutadienes, particularly in view of the fact that **7** can be prepared in one step from oxalyl chloride.[5] Furthermore, the condensation of aniline derivatives with **7** allows the preparation of electronically modified imine substituents for which in some cases bis(imidoyl chlorides) are available only with difficulty (Table 1).[8]

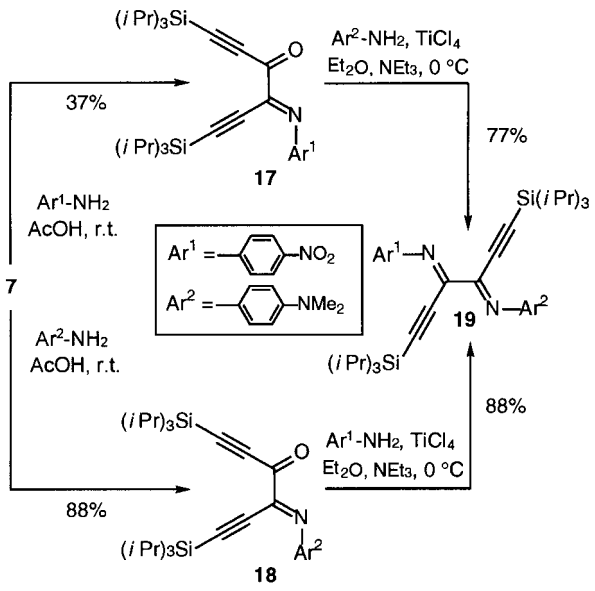
While in general, diimine formation from **7** proceeds smoothly in refluxing xylene, the use of glacial acetic acid as a reaction medium was found to be beneficial in terms of reaction time and yield (cf. formation of **8**, **11**, and **12**). In case of the acid-sensitive methoxy derivative **14**, the yield could be significantly increased by using a $TiCl_4$-mediated imine-formation procedure. This Lewis acid-promoted condensation reaction turned out to be the method of choice for generating *N*-(*p*-CF_3-phenyl)-substituted dialkynyl diazabutadiene **16**, for which all other modes of preparation had failed. The 2,3-dialkynyl 1,4-diazabutadienes are solid, air stable materials whose colors range from yellow (**8** - **12**, **14**, **16**) over orange (**15**) to red (**13**).[9]

The good directing properties and the retarding influence of the triisopropylsilyl groups in the formation of dialkynyl diazabutadienes from **7** is also evident from the fact that the twofold imine formation can be controlled to provide differently *N*-substituted push-pull diazabutadienes.

Table 1. Condensation of **7** with aromatic amines Ar-NH_2

Ar	Method[a]	t[h]/T[°C]	Product	Yield [%][b]
phenyl	A	10 / 140	**9**	70
p-tolyl	A	10 / 140	**10**	65
3,5-dimethylphenyl	A	10 / 140	**8**	70
3,5-dimethylphenyl	B	0.5 / r.t.	**8**	80
2,6-dimethylphenyl	B	2 / 118	**11**	81
2,6-diisopropylphenyl	B	2 / 118	**12**	77
4-Me_2N-phenyl	A	16 / 140	**13**	55
4-MeO-phenyl	A	16 / 140	**14**	48
4-MeO-phenyl	C	0.25 / 0	**14**	55
4-NO_2-phenyl	A	48 / 140	**15**	60
4-CF_3-phenyl	C	16 / 0	**16**	60

[a] Method A: xylene, cat. LiBr; Method B: glacial AcOH; Method C: diethyl ether, $TiCl_4$, NEt_3. [b] yields of isolated product



Hence, reacting **7** with one equiv. *p*-dimethylamino aniline or with one equiv. *p*-nitroaniline yields the iminoketones **17** and **18**, respectively, which serve as intermediates en route to unsymmetrical dialkynyl diazabutadiene **19**, prepared by a subsequent $TiCl_4$-promoted condensation with one equiv. of the corresponding second aniline. It is noteworthy that the greater nucleophilicity of *p*-dimethylamino aniline combined with the tendency of **17** to decompose on silica gel renders the preparation of **19** via **18** the synthetically more useful route. Compound **19**[9] is a deep red microcrystalline solid with a gold-green metallic luster.

The present work has established 1,6-bis(triisopropylsilyl)hexa-1,5-diyne-3,4-dione **7** as a valuable precursor to various 2,3-dialkynyl 1,4-diazabutadienes. An in-depth evaluation of their structural, chemical, and electrochemical properties as well as an investigation of their coordination chemistry is under way.

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(7) The presence of the weak Lewis acid LiBr appears to be mandatory for the successful conversion of **7** to 1,2-diimines by method A.

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(9) *Typical procedure for method A*: A mixture of dialkynyl-1,2-dione **7**[5] (1 mmol), the corresponding aniline derivative (3 mmol), a catalytic amount of LiBr, and activated molecular sieves was refluxed in dry xylene (25 ml) for the time specified in Table 1. After filtration and removal of the solvent the residue was chromatographed on SiO_2 using hexane/ethyl acetate (20/1). *Typical procedure for method B*: To a solution of **7**[5] (1 mmol) in glacial acetic acid (25 ml) was added the aniline derivative (3 mmol) and the solution subjected to the conditions specified in Table 1. After completion of the reaction, the mixture was poured into water (100 ml) and the solution extracted with diethyl ether. The crude product remaining after drying over Na_2SO_4, filtration, and removal of the solvent was chromatographed on SiO_2 using hexane/ethyl acetate (20/1). *Typical procedure for method C*: To a solution of **7**[5] (1 mmol), the aniline derivative (3 mmol), and NEt_3 (2 ml) in diethyl ether (50 ml) under an argon atmosphere was added an etheral solution (10 ml) of $TiCl_4$ (1 mmol) while cooling with an ice-bath. After completion of the reaction (Table 1) the mixture was filtered through a pad of silica gel and the solvents were removed *in vacuo*. The crude product was chromatographed on SiO_2 using hexane/ethyl acetate (20/1). All new compounds were fully characterized and gave correct microanalytical data. See, for example, selected spectroscopic data for (**10**): yellow solid, m.p. 109 °C. – IR (KBr): ν = 2154 (w, C≡C), 1577 cm^{-1} (s, C=N). – UV (CH_2Cl_2): λ_{max} (ε) = 252 (16400), 384 nm (9700). ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 7 Hz, 4 H), 7.15 (d, *J* = 7 Hz, 4 H), 2.35 (s, 6 H, CH_3), 1.03 (s, 42 H, Si(*i* Pr)$_3$). – ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ = 148.7 (C), 147.5 (C), 136.0 (C), 129.0 (CH), 121.7 (CH), 104.0 (C≡C), 98.5 (C≡C), 21.1 (CH_3, arom.), 18.5 (CH_3, Si(*i* Pr)$_3$), 11.2 (CH, Si(*i* Pr)$_3$). – MS (70 eV), *m/z* (%): 596 (60) [M^+], 581 (6) [M^+- CH_3], 554 (2) [M^+- *i* Pr], 298 (100) [M^+/2]. – $C_{38}H_{56}N_2Si_2$ (596.40): calcd. C 76.46, H 9.46 N 4.70; found C 76.37, H 9.64 N 4.64. For (**19**): deep red

solid, m.p. 102 °C. – IR (KBr): ν = 2145 (w, C≡C), 2136 (w, C≡C), 1604 (s, C=N), 1574 cm^{-1} (s, C=N). – UV (CH_2Cl_2): λ_{max} (ε) = 258 (17800), 302 (sh, 11500), 468 nm (18400). – ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 9 Hz, 2 H), 7.90 (d, *J* = 9 Hz, 2 H), 7.10 (d, *J* = 9 Hz, 2 H), 6.68 (d, *J* = 9 Hz, 2 H), 1.14 (s, 42 H, Si(*i* Pr)$_3$), 0.98 (s, 42 H, Si(*i* Pr)$_3$). – ^{13}C-NMR (90.6 MHz, $CDCl_3$): δ = 157.8 (C), 153.2 (C), 150.9 (C), 144.5 (C), 139.7 (C), 137.5 (C), 127.4 (CH), 124.5 (CH), 120.5 (CH), 111.3 (CH), 105.9 (C≡C), 105.1 (C≡C), 100.0 (C≡C), 97.7 (C≡C), 40.3 (CH_3, NMe_2), 18.6 (CH_3, Si(*i* Pr)$_3$), 18.4 (CH_3, Si(*i* Pr)$_3$), 11.3 (CH, Si(*i* Pr)$_3$), 11.1 (CH, Si(*i* Pr)$_3$). – MS (70 eV), *m/z* (%): 656 (100) [M^+], 613 (2) [M^+- *i* Pr], 329 (10) [M^+/2, NO_2-half], 327 (100) [M^+/2, NMe_2-half]. – $C_{38}H_{56}N_4O_2Si_2$ (656.39): calcd. C 69.47, H 8.60 N 8.53; found C 69.26, H 8.54 N 8.67.