with a vacuum pump and purged with nitrogen, and the procedure was repeated several times. Sodium methoxide (4.4 M, 650 μL) was injected dropwise via syringe. The reaction was stirred for 5 h at room temperature under nitrogen. The reaction mixture was concentrated to dryness and treated with water. The product was extracted with ethyl acetate, washed with 2.5 N HCl, and dried ($MgSO_4$), and the solution was evaporated to dryness in vacuo to give 220 mg of crude product. This was chromatographed on HPLC (M-10 10/50 Partisil 10 silica column) and eluted with 60:40 acetone/hexane. The minor first eluted material, after crystalline from ethyl acetate, afforded 26.0 mg; mp 147–148 °C; ^{1}H NMR ($CDCl_3$) δ 1.20 (18 CH_3), 0.90 (19 CH_3), 1.14 (t, 3 H, CH_3CH_2N), 1.15 (t, 3 H, CH_3CH_2N), 1.77 (d, J = 7.0 Hz, 3 H, ($CH_3CH{=}$), 2.45 (m, H_2), 2.82 (d, d, J = 5 and 16 Hz, 1 H), 2.95 (s, NCH_3), 3.04 (d, d, J = 13.0 and 3 Hz, 1 H, H_5), 3.20–3.45 (m, CH_3CH_2N), 6.91 (q, t, J = 7.3 Hz, 1 H, $CH_3CH{=}$); MS, *m/e* found M^+ 442.31818 corresponding to empirical formula $C_{27}H_{42}N_2O_3$, calcd M^+ 442.3193. This material appears to be the 16-ethylidene derivative of the ketone **6**.

The major product **6** was isolated (85.0 mg): mp 156–158 °C; ^{1}H NMR ($CDCl_3$) δ 0.90 (19 CH_3), 1.14 (t, J = 6.0 Hz, 3, CH_3CH_2N), 1.15 (t, J = 6.0 Hz, 3 H, CH_3CH_2N), 1.20 (18 CH_3), 2.53 (m, 2 CH_2), 3.02 (s, NCH_3), 3.12 (d, d, J = 13.5 and 3.5 Hz, 5-CH), 3.21 (m, NCH_2CH_3), 3.49 (m, NCH_2CH_3), 3.40 (s, 1, 17a-CH); MS, *m/e* found M^+ 416, calcd H^+ 416 for $C_{25}H_{40}N_2O_3$.

Anal. Calcd for $C_{25}H_{40}N_2O_3\cdot{}^1/_5H_2O$: C, 71.45; H, 9.69; N, 6.67. Found: C, 71.21; H, 9.59; N, 7.05.

Equilibrium Studies of β-Isomer 6 and α-Isomer 5. A solution of 12.6 mg of β-isomer **6** and 12.0 mg of potassium acetate in 10.0 mL of methanol was refluxed under nitrogen for 20 h. The reaction mixture was concentrated to dryness. The product was extracted into ethyl acetate, washed with water, dried ($MgSO_4$), and isolated as a solid. The product mixture was analyzed by HPLC on a Porosil column and by measurement of the C-18 methyl peak heights in the NMR. In this way **5** separated from **6** in a ratio of 2:1 favoring the α-isomer.

Similarly, the α-isomer (12.6 mg) was treated as above, and again **6** separated from **5** in a ratio of 2:1 favoring the α-isomer.

Deuterium Incorporation in α-Isomer 5. Isopropylamine (10.5 μL) was dissolved in 0.3 mL of dry tetrahydrofuran, the mixture was purged with nitrogen, and the solution was treated dropwise at −78 °C with BuLi (34.1 μL, 22 mM). After 45 min at −78 °C, α-isomer **5** (10.0 mg) in 0.3 mL of tetrahydrofuran was added via syringe. The reaction was stirred at this temperature for 1 h under nitrogen, followed by quenching with 0.5 mL of CD_3COOD. The reaction mixture was concentrated to dryness; the product was extracted in ethyl acetate, washed with water and with saturated aqueous NaCl, dried ($MgSO_4$), and isolated as a white solid. The product isolated had a retention time on HPLC identical with the α-isomer **5**. The proton NMR of the isolated product indicates that the deuterium incorporation has been localized primarily at C_{16} δ 3.00 and C_2 2.43. Surprisingly, no appreciable exchange has occurred at C_{17a} δ 3.26 based on inspection and area measurement.

As far as can be determined from relative areas, 0.3–0.5 D was introduced at C_{16} and has involved exclusively the lower field proton of the genuinely nonequivalent pair. The area of the 2-CH_2 appears to be about 20% below stoichiometry which corresponds to roughly the introduction of 0.4 D. The estimated total deuterium incorporation thus is reasonably compatible with the net mass spectral finding of one deuterium.

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Registry No. **1**, 92472-87-2; **2**, 92763-04-7; **3**, 92786-69-1; **5**, 92763-05-8; **6**, 92763-06-9; **6** (16-ethylidene deriv), 92763-07-0.

Supplementary Material Available: Table 1, fractional coordinates and temperature factors for structure **5**; Table 2, bond distances; Table 3, bond angles (3 pages). Ordering information is given on any current masthead page.

1,6-Bis(trimethylsilyl)hexa-1,5-diyn-3-ene: Models To Determine the Structure of Polydiacetylenes

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The title compound (**1**, as both cis and trans isomers) is the protected form of a synthon (hexa-1,3-diyn-2-ene, **2**) which has been of some interest and importance in physical organic and organometallic chemistry.[1-3] We also believe the title compound to be of value in the preparation of organic compounds of interest in solid state organic chemistry; for example, deprotection of **1** would lead to an immediate precursor to the elusive parent "polydiacetylene". Polydiacetylenes (PDA's) are polymers whose backbone consists of alternating double and triple bonds. To date only PDA's with large substituents on the ene portion of the backbone have been prepared by a solid state polymerization reaction of 1,4-disubstituted butadiynes.[4] Diacetylene itself polymerizes but does not afford the regular polymer described above for the substituted diacetylenes.[5] Attempts have been made to convert substituted PDA's to organic conductors via redox reactions ("doping"), but only very moderate increments in conductivity have been reported,[6] probably due to interference (steric, chemical, or electronic) of the substituents. It would therefore be highly desirable to be able to prepare the parent PDA (prepared by alternate procedure) to test whether indeed it could be doped to levels of metallic conductivity.

Compound **2** could also be a precursor to a large number of organic molecules containing a hexatriene of known stereochemistry and ultimately a polyene via hydroboration followed by functional group interconversion. These transformations have been carried out in our group and will be the subject of future publications.[7]

In this paper we report a very simple procedure for the preparation of **1** and **2** and full characterization of each individual isomer of **1**. The latter turned out to be of considerable importance in the structure determination of certain solvatochromic PDA's.[8]

Results and Discussion

The most recent synthesis of **2** is still multistep and affords a difficult-to-separate mixture of isomers. The isomer separation and purification are hampered by extreme instability of this highly unsaturated molecule.[1,2] We

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Table I

no.	IR	^{1}H NMR (δ, Me$_4$Si)	^{13}C NMR (δ, Me$_4$Si)	UV–vis[e]	MS
1a	3040 w, 3020 w, 2958 s, 2150 s, 2120 m, 1745 m, 1565 w, 1455 w, 1405 w, 1385 m, 1240 s, 1200 w, 1065 s, 920 s, 840 s, 755 s, 695 m, 630 s, 500 w[a]	5.98 (s, 2 H), 0.23 (s, 18 H)[b]	121.49 (d, J_{C-H} = 169 Hz), 103.37 (s), 102.94 (m), 0.57 (q)[b]	288.4 (ϵ 2.78 × 10^4), 272.4 (ϵ 2.44 × 10^4)	calcd 220.1103, found 220.1103
1b	3015 w, 2938 s, 2158 s, 2110 s, 1748 m, 1440 w, 1400 m, 1240 s, 1085 s, 720 s, 830 s, 745 s, 685 s, 625 s, 470 s, 318 s[c]	6.18 (s, 2 H), 0.13 (s, 18 H)[d]	121.96 (d, J_{C-H} = 165.2 Hz), 103.6 (s), 101.07 (s), –0.15 (q)[b]	287.5 (ϵ 4.08 × 10^4), 271.3 (ϵ 3.67 × 10^4)	calcd 220.1103, found 220.1104

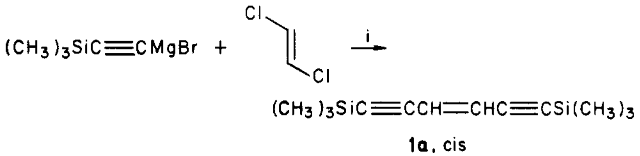
[a] Neat film. [b] $(CD_3)_2CO$. [c] KBr. [d] C_6D_6. [e] THF.

have prepared both isomers of 1 in good yield according to Scheme I.[9]

Deprotection of 1 to 2 was carried out with methanol and hydroxide, fluoride, or hydride ion catalysis. It was found that 2 decomposed, forming a colored solution in THF in concentrations greater than 0.01 M. Therefore solutions of 2 were always maintained at low concentration and quantitated spectroscopically. Separation of the diastereomers (**1a** from **1b**) was unexpectedly facile since **1b** turned out to be a solid and **1a** is liquid. The latter could be obtained analytically pure by thick layer chromatography on silica gel. Some properties of these molecules are collected in Table I. Deprotection of **1b** produced pure *trans*-enediyne **2** identical in all respects with properties previously reported.[3]

It was recently stated that, at least in a certain family of PDA's, the backbone was of all trans configuration as determined by ^{13}C NMR. This conclusion was predicated on a set of experiments which involved comparing solid state and solution spectra as well as an assumption that the chemical shifts of the *cis*- and *trans*-alkene regions would differ by about the same amount as in polyacetylene ($\simeq$10 ppm).[10] We reasoned that not only was it dangerous to compare solid state with solution spectra but that the change in chemical shift with stereochemistry of an alkene may in fact depend on the substituents. Our title compounds were ideally suited to test the latter. As can be seen from the table, the chemical shifts of the sp^2 hybridized carbons of **1a** and **1b** differ by only ca. 1 ppm, making it rather difficult to assign configuration to the backbone of a PDA on the basis of ^{13}C NMR spectroscopy. It is also interesting to note that the chemical shifts of all unsaturated carbons in compounds 1 are *deshielded* relative to polyacetylene or fully carbon-substituted PDA's[10,11] by ca. 6–10 ppm. This result leads us to suggest that the trimethylsilyl groups are responsible for the deshielding effect.[12]

Scheme I[a]



1a, cis
1b, trans

[a] i = $Cl_2Ni(dppp)$; dppp = $Ph_2P(CH_2)_3PPh_2$.

Experimental Section

Preparation of 1a and 1b. A solution of 12.51 g (0.126 mol, 18 mL) of $(CH_3)_3SiC{\equiv}CH$ in 100 mL of dry THF was cooled to –78 °C. To this solution was slowly added 42 mL (0.121 mol) of 2.9 M methyl magnesium bromide in ether. The thick white suspension was then allowed to warm to room temperature over a period of 2 h, and then the reaction mixture was gently boiled under an atmosphere of argon for 1 h. After cooling the reaction vessel to –78 °C, 4.89 g (0.0504 mol., 3.88 mL) of *trans*-$CHCl{=}CHCl$ and 0.92 g (0.0017 mol) of $NiCl_2$(dppp) were added in sequence to the reaction mixture. The reaction mixture was then slowly warmed to room temperature, the color of the mixture first turned lemon yellow and then finally a dark red-brown. After 12 h the reaction was quenched by pouring the mixture into saturated aqueous NH_4Cl. The organic phase was separated from the aqueous phase and then washed with H_2O and brine. After drying the organic phase with Na_2SO_4 and evaporating the solvent, a yellow-white semicrystalline solid in a brown oil was obtained. The entire product was then dissolved in 40 mL of hexane and filtered through a 10 × 2 cm column of neutral alumina. The column was rinsed with an additional 60 mL of hexane, and the combined fractions were evaporated, leaving a yellow-white solid in a yellow oil. Recrystallization of the product from MeOH produced 7.70 g (70%) of **1b**. An analytically pure sample was obtained by preparative TLC (SiO_2, hexanes) followed by recrystallization from isopentane; mp 72 °C. Anal. Calcd for $C_{12}H_{20}Si_2$: C, 65.38; H, 9.15; Si, 25.48. Found: C, 65.28; H, 9.14; Si, 25.08. The mother liquor from the original recrystallization of **1a** was evaporated and was found to contain a mixture of **1a** and **1b** as verified by TLC and ^{1}H NMR. A spectroscopically pure sample (see Table I) of **1a** could be obtained as a yellow oil by multiple preparative TLC (SiO_2, hexanes).

Preparation of Solutions of 2. A typical procedure for the dideprotection of **1b** involved the addition of a catalytic amount of sodium hydride to **1b** (0.364 g, 1.65 mmol) and methanol (0.11 g, 3.3 mmol) in 200 mL of dry THF. Progress of the deprotection was followed spectrophotometrically. On complete conversion to **2**, tolylene 2,4-diisocyanate was added to react with any unreacted methanol. The volatiles were then distilled into a cold receiver under inert atmosphere. The solution gave λ_{max} (THF) 254 nm (ϵ 2.5 × 10^4), 264 (ϵ 2.3 × 10^4), in good agreement with results reported by Sondheimer.[3]

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Registry No. **1a**, 92787-97-8; **1b**, 92787-96-7; **2**, 16668-68-1; $NiCl_2$(dppp), 15629-92-2; $(CH_3)_3SiC{\equiv}CMgBr$, 61210-52-4; $(CH_3)_3SiC{\equiv}CH$, 1066-54-2; *trans*-$CHCl{=}CHCl$, 156-60-5.

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(12) This effect may be due to back-donation from the alkyne π orbitals to Si d orbitals.