SYNTHESIS AND REACTIONS OF 3-(5-DICYCLOPENTADIENYL)-1-TRIMETHYLSILYLPROPYNE

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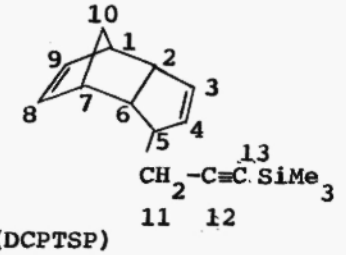
ABSTRACT

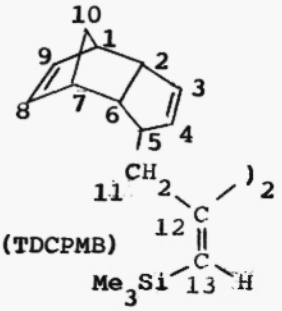
3-(5-Dicyclopentadienyl)-1-trimethylsilylpropyne (DCPTSP) has been synthesized from endo-anti-5-chlorotricyclo [5.2.1.$0^{2,6}$] deca-3, 8-diene (DCPCl) on reaction with 1-trimethylsilylpropyne. This novel silylated tricyclic compound has been used to synthesize 1.4- bis (trimethylsilyl)-2,3-bis (5-dicyclopentadienylmethyl) 1,3-butadiene (TDCPMB) and 3-(5-dicyclopentadienyl)-1-propyne (DCPP).

INTRODUCTION

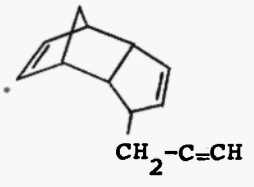
Trimethylsilyl substituted alkynes are an important class of compounds. They give metallacycles on reaction with metallocene dihalides [1,2] and degradation of such metallacycles produce stereoselective silyl compounds [1,3]. In the present work we report a three step synthesis of a novel silyl-protected alkyne (DCPTSP) from DCPCl. In addition two compounds, TDCPMB and DCPP have been synthesised form DCPTSP.



(DCPTSP)



(TDCPMB)



(DCPP)

EXPERIMENTAL

Materials and Solvents: Diethylether, tetrahydrofuron, 1-trimethylsilylpropyne, hexamethylphosphoric triamide (HMPA) and N,N,N',N'-tetramethylethylenediamine (TMED) were freshly distilled before use. Endo-anti-5-chlorotricylo[5.2.1.$0^{2,6}$]deca-3,8-diene (DCPCl) was prepared by the procedure of Dilling et al [4].

Physical Methods: ^{1}H and ^{13}C NMR spectra were recorded on a varian VXR-300 spectrometer using $CDCl_3$ as a solvent. Infra-red spectra were taken on a Perkin-Elmer 710B spectrophotometer. Elemental analyses were determined by Schwartzkopf Microanalytical Laboratory, Inc. Woodside, NY.

Synthesis of 3-(5-dicyclopentadienyl)-1-trimethylsilylpropyne (DCPTSP)

n-Butyllithium (48 ml, 0.12 mol) was placed in a one litre three necked round bottom flask equipped with a thermometer, a rubber septum,

a magnetic stir bar and an argon gas adaptor. This solution was cooled to -15 °C and 200 ml of anhydrous argon flushed ether, TMED (18.1 ml, 0.12 mol) and 1-trimethylsilylpropyne (18.5ml, 0.12 mol) were successively added. The solution was stirred at -15 °C for 4 h. after which the mixture was cooled to -20 °C and 10.0g (0.06 mol) of DCPCl and 130 ml of HMPA were added slowly. After 12 h. of stirring at -20 °C, the reaction mixture was poured into 300 ml of cold 3N HCl and the product was extracted with excess of ether. The ether extract was dried over anhydrous sodium sulphate. The solvent was removed and the crude product was distilled at 74-76 °C (0.05 torr). 10.47g(71.8%) of a colourless liquid were obtained. Found: C, 79.08: H,9.26; Si, 11.31, C_{16} H_{22} Si Calc: C, 79.26; H, 9.15; Si 11.59%.

Synthesis of 1,4-bis(trimethylsilyl)-2,3-bis (5-dicyclopentadienyl-methyl) 1,3-butadiene (TDCPMB)

To a 250 ml reaction flask, 0.30g (1.0 mmol) of Cp_2ZrCl_2, 0.28g (1.0 mmol) of $HgCl_2$ and 0.1g (4.1 mmol) of Mg powder were added under argon. 40 ml of THF was added along with 0.5g (2.0 mmol) of DCPTSP. The reaction mixture was stirred for 12 h. at room temperature. The solvent was removed under vacuum and the residue dissolved in pentane and filtered over Celite in a glove box. Removal of pentane gave a mixture of an orange crystalline solid and a viscous liquid. Attempts to isolate a pure metallacyclic compound from the mixture failed. The crude product was dissolved in ether and 50 ml of dil. HCl was added. The mixture was stirred for 15 min. and the organic layer was separated, washed with saturated sodium bicarbonate and dried over anhydrous sodium sulphate. Removal of ether gave crystalline product which was purified by column chromatography on silica gel. Elution with pentane gave a colourless product (0.32g, 63.6%). Found: C,78.69; H, 9.56; Si, 11.34, C_{32} H_{46} Si_2 Calc: C, 78.93;H, 9.52; Si, 11.54%.

Synthesis of 3-(5-dicyclopentadienyl)-1-propyne (DCPP)

3.0g (12.3 mmol) of 3-(5-dicyclopentadienyl)-1-trimethylsilyl-propyne in ethanol was added slowly to a silver nitrate (3.1g, 18.2 mmol) solution in ethanol/water at room temperature with constant stirring. The white precipitates formed were dissolved by addition of potasssium cyanide (5.6g, 86.1 mmol) in water. The reaction mixture was stirred for one hour and then poured into water. The product was extracted with petroleum ether, dried over anhydrous sodium sulphate and then distilled under reduced pressure to yield 1.62g (77.1%) of pure 3-(5-dicyclopentadienyl)-1-propyne. Found: C, 91.57; H, 8.21, C_{13} H_{14} Calc: C, 91.71; H, 8.29%.

DISCUSSION

DCPTSP has been synthesised in high yield (71.8%) from DCPCl. The product was characterized by elemental analysis, IR, ^1H and ^{13}C studies. The ^1H NMR signals of DCPTSP are assigned in comparison with the ^1H NMR parameters of DCPCl[4]. 2D NMR studies on bis (η^5-cyclo-pentadienyldicyclopentadiene) hafnium dichloride [5] and ferrocene complex of tricyclo [5.2.1.$0^{2,1}$] deca- 2,5-8-triene [6] also helped in NMR assignments. Proton decoupled ^{13}C NMR signals were assigned with the aid of DEPT spectra. Signals arising from C_{12} and C_{13} disappear in the DEPT and are assigned to quaternary carbons. Infra-red spectra of the compound show prominent characteristic bands at 2170 (C=C) and 1255, 845 cm^{-1} (Me_3Si).

TDCPMB was synthesised from DCPTSP using $Cp_2ZrCl_2/Mg/HgCl_2$.

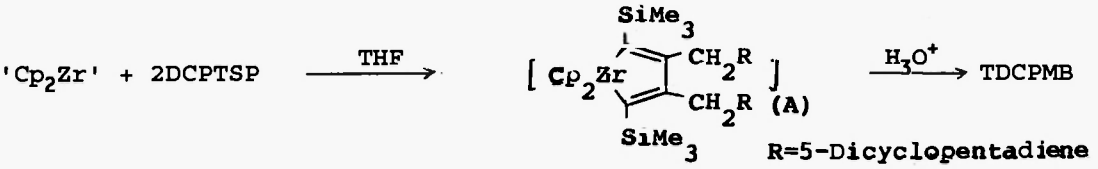


Table -1: ^1H and ^{13}C NMR spectral data of DCPTSP and TDCPMB

Compounds	Assignments, δ (ppm)
DCPTSP	**^1H NMR:** 0.13(s, $SiMe_3$), 1.29(d, H_{10}, J= 7.8Hz) 1.47(d, $H_{10'}$, J = 7.8 Hz), 2.11 - 2.20 (m, $H_{6,11}$), 2.40(m, H_2), 2.78 (s*, H_1), 2.90 (s*, H_7), 3.21 (m, H_5) 5.46, 5.54 (d,$H_{4,3}$, J = 5.8Hz), 5.90, 5.96 (dd, $H_{9,8}$) **^{13}C NMR:** 0.18 ($SiMe_3$), 26.99 (C_{11}), 50.27 (C_{10}),46.08, 46.82, 47.43, 48.58 ($C_{1,5,6,7}$) 54.81 (C_2), 84.83 (C_{13}), 106.63 (C_{12}), 132.86, 133.29 ($C_{3,4}$) 135.06, 135.75 ($C_{8,9}$)
TDCPMB	**^1H NMR:** 0.12 (s, $SiMe_3$), 1.24 (d, H_{10}, J = 7.8 Hz),1.44 (d, $H_{10'}$, J = 7.8 Hz), 1.90 - 2.25 (m, $H_{6,11}$), 2.32 (m, H_2), 2.73 (s*, H_1), 2.78 (s*, H_7), 3.19 (m, H_5), 5.40, 5.46 (dt, $H_{3,4}$, J = 5.7, 1.7 Hz) 5.58 (s, H_{13}), 5.85 (t, $H_{8,9}$, J = 1.7 Hz) **^{13}C NMR:** 0.53 ($SiMe_3$), 40.60 (C_{11}), 50.42 (C_{10}),45.13, 46.34, 46.61, 47.25 ($C_{1,5,6,7}$), 54.42 (C_2), 127.78 (C_{13}) 162.19 (C_{12}), 131.99, 132.70 ($C_{3,4}$), 135.57, 136.42 ($C_{8,9}$)

s = Singlet, s* = singlet that tends to split further, d = doublet, t = triplet, m = complex pattern, dd = doublet of doublet.

TDCPMB is a colourless crystalline compound (m.p. 119-121 °C). This product is believed to result through a metallacyclic inter-mediate (A). The intermediate in this case being unstable could not be isolated, however in earlier work on relatively simple reactions [7] we isolated silyl substituted metallacycles which on protonolysis gave E, E-1,4-bis(trimethylsilyl) butadienes. The metallacyclic inter-mediate (A) when treated with dil. HCl released the E,E-isomer of 1,4-bis(trimethylsilyl)-2,3-bis(5-dicyclopentadienylmethyl)1,3-butadiene. This is expected since reactions of a variety of metallacyclopenta-dienes with HCl led to the recovery of exclusively E,E isomers[7-9]. ^1H and ^{13}C NMR signals for TDCPMB are assigned in Table-1. DEPT spectra helped in ^{13}C NMR assignments. The ^1H NMR of TDCPMB as compared to that of DCPTSP shows an additional signal at 5.5 ppm (singlet) due to the olefinic H_{13}, which confirms the conversion of alkyne to olefin through the metallacyclic intermediate. This is further confirmed by ^{13}C NMR studies of the two compounds. C_{12} and C_{13} in TDCPMB resonate at 162.19 and 127.78 ppm while in DCPTSP at 106.63 and 84.83 respectively. Reported ^{13}C NMR data on 2,3-dimethyl-1,3-butadiene and 1,4-bis(trimethylsilyl)-2,3, dimethyl-1,3-butadiene[8,10] also support ^{13}C assignments of TDCPMB.

3-(5-dicyclopentadienyl)-1-propyne (DCPP) was synthesised from DCPTSP in high yield and was characterized by elemental analysis, IR and ^1H NMR studies. The characteristic IR stretching bands include 2130 (C≡C)

and 3300 cm^{-1} (C≡C-H). The ^1H NMR of DCPP resembles that of DCPTSP except that a new signal appears at 1.90 ppm which is assigned to the acetylenic hydrogen [11] and resonance of Me_3Si disappears.

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