

TITANIUM-CATALYZED DIELS-ALDER ADDITION OF BIS(TRIMETHYLSILYL)ACETYLENE TO 1,3-CYCLOHEXADIENE

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Received December 27, 1988

Accepted January 4, 1989

Dedicated to late Academician Eduard Hála.

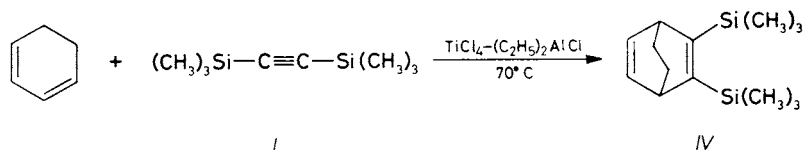
The $\text{TiCl}_4-(\text{C}_2\text{H}_5)_2\text{AlCl}$ catalyst induces the Diels-Alder addition of bis(trimethylsilyl)acetylene to 1,3-cyclohexadiene affording 2,3-bis(trimethylsilyl)bicyclo[2.2.2]octa-2,5-diene in 72% yield under mild conditions. The product eliminates ethylene upon heating to 240°C to give 1,2-bis(trimethylsilyl)benzene.

The synthetic potential of bis(trimethylsilyl)acetylene (*I*) in cycloaddition reactions catalyzed by transition metal complexes has been reviewed¹. We have found that the [4 + 2] and [6 + 2] cross-additions of *I* to linear conjugated dienes and to 1,3,5-cycloheptatriene, respectively, are catalyzed by the $\text{TiCl}_4-(\text{C}_2\text{H}_5)_2\text{AlCl}$ system under mild conditions^{2,3}. The high efficiency of this preparative method was a result of the formation of a stable complex between titanium and *I* which activated both reagents and suppressed the activity of the catalytic system for homopolymerization of dienes and dimerization of cycloheptatriene. Analogous addition of *I* to norbornadiene yielded two isomeric products, 2,3-bis(trimethylsilyl)-*cis*-bicyclo[4.3.0]nona-2,4,8-triene (*II*) and 3,4-bis(trimethylsilyl)-*cis*-bicyclo[4.3.0]nona-2,4,8-triene (*III*) in cascades of electrocyclic reactions⁴. The yields of the individual products varied strongly in dependence on the conditions for formation of the catalytic system. Rapid warming to 20°C of the reaction mixture previously mixed at -50°C afforded *II*, whereas warming to 60°C gave *III*. In this communication we describe the catalytic preparation of a dihydrobarrelene derivative from 1,3-cyclohexadiene and *I*.

RESULTS AND DISCUSSION

The $(\text{C}_2\text{H}_5)_2\text{AlCl-TiCl}_4$ catalyst (Al : Ti = 15) induces [4 + 2] cycloaddition of *I* to 1,3-cyclohexadiene affording 2,3-bis(trimethylsilyl)bicyclo[2.2.2]octa-2,5-diene (*IV*). The yield as high as 72% of isolated *IV* was obtained if the complex between

titanium reduced to a low valent state and *I* was formed²⁻⁴ prior to addition of 1,3-cyclohexadiene (Scheme 1). This yield corresponded to the turnover *I* : Ti = 50. No volatile byproducts were formed; a trace amount of the distillation residue was, according to infrared spectra, the homopolymer of 1,3-cyclohexadiene. In contrast,



SCHEME 1

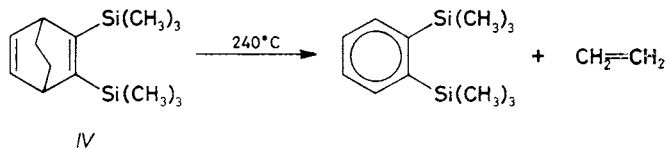
addition of 1,3-cyclohexadiene to the catalytic system before *I* or together with it led to only 30% conversion of *I* to *IV*. The main product was the polymer of 1,3-cyclohexadiene containing incorporated units of *I* as judged from the presence of absorption bands characteristic of the trimethylsilyl group in the IR spectrum. In the absence of *I* the 1,3-cyclohexadiene polymer was formed quantitatively. No dimer of 1,3-cyclohexadiene was distilled off from the polymer at 100°C in high vacuum.

Product *IV* was obtained in better than 97% purity (GC MS analysis) by vacuum distillation of the reaction solution after decomposition and removal of the catalyst components. The structure *IV* was deduced from MS, ¹H and ¹³C NMR and IR spectra. The MS spectrum did not show the M⁺⁺ ion (*m/z* 254) but the ions (M - H)⁺, (M - 2H)⁺⁺, (M - 3H)⁺ and (M - 4H)⁺⁺ in successively increased intensities (*m/z* 250, 12%). The retro-Diels–Alder fragmentation was the main decomposition pathway upon electron impact (*m/z* 80, C₆H₈⁺, 100%). The NMR spectra revealed the presence of six equivalent CH₃ groups, two pairs of *sp*² carbon

atoms ($\begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ =\text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{Si} \end{array}$ and $\begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ =\text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{H} \end{array}$) and two pairs of *sp*³ carbon atoms (CH₂ and CH).

The IR spectrum confirmed the presence of two different double bonds in the $\nu(\text{C}=\text{C})$ region, one CH=CH group in the $\nu(\text{C}-\text{H})$ region and the Si(CH₃)₃ groups.

The cycloaddition reaction is strongly influenced by the presence of substituents in the cyclohexadiene molecule. Attempts to induce the Diels–Alder addition of *I* to α -phellandrene, 2-methyl-5-isopropylcyclohexa-1,3-diene, using this catalyst gave a low yield (approx. 10%) of products distillable in vacuo and a polymer. According to GC MS analysis, the complex mixture of products contained *p*-cymene, the expected Diels–Alder adduct and the hydrogenated adduct. It shows that the Diels–Alder addition is accompanied by easy hydrogen transfer from α -phellandrene to the Diels–Alder adduct and competes with the α -phellandrene polymerization.



SCHEME 2

Heating of *IV* to 240°C for 3 h afforded 1,2-bis(trimethylsilyl)benzene practically quantitatively with elimination of ethylene (see Scheme 2). The distilled product gave identical MS, ^1H and ^{13}C NMR and IR spectra to the authentic sample prepared by thermally induced hydrogen molecule elimination from 1,2-bis-(trimethylsilyl)-cyclohexa-1,4-diene³. The above reaction, known as an Alder–Rickert reaction⁵, has so far been observed with derivatives containing strongly polar substituents⁶. The absence of 1,2-bis(trimethylsilyl)-3-ethylbenzene as a product of thermolysis of *IV* indicates that ethylene elimination is a concerted reaction.

EXPERIMENTAL

Chemicals. Bis(trimethylsilyl)acetylene (Fluka) was degassed and distilled in vacuo. 1,3-Cyclohexadiene (Fluka) was distilled in vacuo onto solid dimeric titanocene⁷ and allowed to stay for 3 days. The known volumes of both reagents were distilled into breakable seal ampoules in vacuo. Benzene (Fluka) was shaken with sulfuric acid, dried over LiAlH_4 , and purified by the same procedure as that for 1,3-cyclohexadiene. TiCl_4 (International Enzymes) was distilled in vacuo and diluted with benzene to give a 0.1M solution. $(\text{C}_2\text{H}_5)_2\text{AlCl}$ (Fluka) was purified from traces of the sesquichloride by heating with anhydrous sodium chloride to 180°C; it was then distilled in vacuo and diluted with benzene to give 1.0M solution. The solutions of the catalyst components were distributed in vacuo into ampoules equipped with breakable seals and sealed in.

Methods. Mass spectra were recorded on a Jeol JMS D-100 spectrometer at 75 eV, using either a direct inlet or the gas chromatograph — mass spectrometer coupling. ^1H and ^{13}C NMR spectra were measured on a Varian VXR-400 instrument (400 MHz and 100 MHz, respectively) in deuteriochloroform with tetramethylsilane as an internal standard at 25°C. Chemical shifts are expressed in the δ (ppm) scale. Infrared spectra were recorded in thin liquid film on a UR-75 (Zeiss, Jena) spectrometer.

2,3-Bis(trimethylsilyl)bicyclo[2.2.2]octa-2,5-diene (*IV*)

TiCl_4 (2 ml of 0.1M solution in benzene) and $(\text{C}_2\text{H}_5)_2\text{AlCl}$ (6 ml of 0.5M solution in benzene) were mixed in an evacuated ampoule and, after warming to 70°C for 5 min, *I* (2.3 ml, 10.4 mmol) was added. After warming to 70°C for 20 min, a green solution was obtained and 1,3-cyclohexadiene (1.0 ml, 10.5 mmol) was introduced at room temperature. The mixture was cooled, the ampoule was sealed out and immersed in a 70°C water bath for 6 h. The mostly homogeneous brown-green reaction mixture was opened to air, poured onto a 7 cm long silica gel column and eluted with hexane. Distillation in vacuo separated the product from the solvent and non-

volatile byproducts. The yield of *IV* (colourless liquid) was 1.85 g, 72% of theory related to *I*. Spectral characteristics of *IV*: MS spectrum (relative intensity higher than 5% and peaks important for m.w. determination: m/z , %): 253, 0.15; 252, 1.3; 251, 2.8; 250, 12.2; 235, 5.3; 207, 10.7; 191, 17.5; 176, 6.7; 171, 8.9; 162, 5.1; 161, 5.5; 155, 18.5; 147, 6.5; 97, 6.4; 83, 5.8; 81, 10.9; 80, 100; 79, 15.1; 74, 6.4; 73, 66.5; 59, 6.6; 45, 17.5; 43, 8.5. ^1H NMR spectrum: 0.220 s (18 H, $2 \times \text{SiMe}_3$); 1.099 mt (2 H); 1.239 mt (2 H); 3.983 mt (2 H); 6.307 dd (2 H, $J = 4.55$ and $J = 3.15$ Hz). ^{13}C NMR spectrum: 0.95 q (6 C), 24.42 t (2 C), 42.79 d (2 C), 133.95 d (2 C), 156.31 s (2 C). IR spectrum (neat; cm^{-1}): 3 048 m, 2 946 s, 2 902 m, 2 866 m, 1 613 w, 1 530 w, 1 458 w, 1 442 w, 1 403 w, 1 347 w, 1 260 s, 1 247 s, 1 153 w, 1 113 vw, 1 076 vw, 1 056 m, 963 m, 940 s, 858 sh, 830 vs, 755 s, 735 w, 701 m, 688 sh, 671 m, 621 m, 553 vw, 505 w, 492 w, 437 m.

Thermolysis of IV. Compound *IV* (0.8 g) was degassed and heated in a 80 cm^3 ampoule at 240°C for 3 h. Ethylene was pumped off and the liquid was distilled in vacuo to give 0.65 g (92%) of 1,2-bis(trimethylsilyl)benzene. Its MS, ^1H and ^{13}C NMR and IR spectra were identical with those of the authentic sample³.

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Translated by the author (K.M.).