TITANIUM-CATALYZED [4+2] and [6+2] CYCLOADDITIONS OF 1,4-BIS(TRIMETHYLSILYL)BUTA-1,3-DIYNE

Jan-Willem F. KAAGMAN[a1], Marco REP[a2], Michal HORACEK[b1], Petr SEDMERA[c],
Jiri CEJKA[b2], Vojtech VARGA[b1] and Karel MACH[b1,*]

[a] *Inorganic Chemistry Laboratory, J.H. van't Hoff Institute, University of Amsterdam,*
1018 WV Amsterdam, The Netherlands; e-mail: [1] janw@anorg.chem.uva.nl,
[2] mrep@anorg.chem.uva.nl
[b] *J. Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic,*
182 23 Prague 8, Czech Republic; e-mail: [1] mach@jh-inst.cas.cz, [2] cejka@jh-inst.cas.cz
[c] *Institute of Microbiology, Academy of Sciences of the Czech Republic, 142 20 Prague 4,*
Czech Republic; e-mail: sedmera@biomed.cas.cz

Received September 5, 1996
Accepted October 23, 1996

The $(C_2H_5)_2AlCl/TiCl_4$ catalyst induces the [4+2] cycloaddition of butadiene or the [6+2] cycloaddition of 1,3,5-cycloheptatriene (CHT) to individual acetylenic moieties of 1,4-bis(trimethylsilyl)buta-1,3-diyne (BSD). Heating of the 2 : 1 butadiene adduct, bis(2-trimethylsilylcyclohexa-1,4-dien-1-yl), to 250 °C yields 2,2′-bis(trimethylsilyl)biphenyl. The 1 : 1 adduct of BSD with CHT, 7-trimethylsilyl-8-trimethylsilylethynylbicyclo[4.2.1]nona-2,4-diene, is obtained as virtually the only product if the initial molar ratio CHT : BD equal to 1.86 is used.

Key words: Titanium catalyst; Cycloadditions; 1,4-Bis(trimethylsilyl)buta-1,3-diyne; 1,3-Butadiene; 1,3,5-Cycloheptatriene.

Bis(trimethylsilyl)acetylene (BTMSA) is a useful reagent in cycloaddition reactions catalyzed by transition metal complexes[1,2]. We have found that it is an excellent dienofile in the Diels–Alder reactions and a trienofile in the [6+2] addition with 1,3,5-cycloheptatriene (CHT), both having been induced by a classical Ziegler–Natta catalyst $Et_2AlCl/TiCl_4$ (refs[3–6]). Analogous reactivity was also found for 1-phenyl-2-(trimethylsilyl)acetylene[7,8]. Both these acetylenes were reluctant to catalytically cyclotrimerize and moreover, they suppressed the property of the catalyst to homooligomerize the dienes or CHT. Another reagent of interest with respect to cycloaddition reactions is 1,4-bis(trimethylsilyl)buta-1,3-diyne (BSD) whose reactivity in general is rather low[9]. It could react as a dieno- or trienofile by one or both triple bonds in a similar way like

---

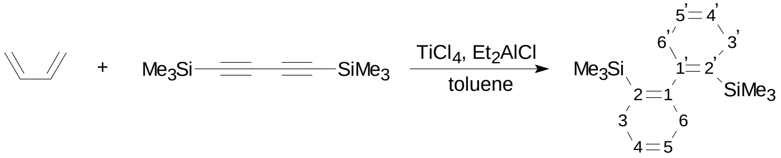
[*] The author to whom correspondence should be addressed.

the above mentioned acetylenes, however, its cobalt-catalyzed cyclotrimerization yielding tris(trimethylsilyl)tris(trimethylsilylethynyl)benzene isomers was also reported[10]. Cleavage of BSD on titanocenes formed *in statu nascendi* has been observed yielding either $[(C_5HMe_4)_2Ti(C{\equiv}CSiMe_3)_2]^-[Mg(THF)Cl]^+$ (ref.[11]) or $[(C_5H_5)_2Ti(C{\equiv}CSiMe_3)]_2$ (ref.[12]).

In this paper we report on the reactivity of BSD towards several conjugated dienes and CHT in the presence of the $Et_2AlCl/TiCl_4$ catalytic system.

RESULTS AND DISCUSSION

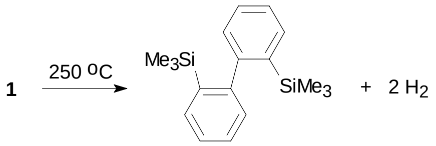
The $(C_2H_5)_2AlCl/TiCl_4$/toluene (Al : Ti = 10) system in the presence of 1,4-bis(trimethylsilyl)-1,3-butadiyne (BSD) at the molar ratio BSD : Ti ≥ 5 gives rise to a brown solution. The system does not induce reactions of BSD alone as it is recovered after quenching the catalyst with air. Additions of conjugated dienes 1,3-butadiene (BUT), 2,3-dimethyl-1,3-butadiene (DMB) or 1,3-cyclohexadiene (CXD) to the above $(C_2H_5)_2AlCl/TiCl_4$/BSD/toluene system afford the products of [4+2] addition, where BSD is a single or double dienofile. In addition, homooligomers and/or polymers of the dienes are formed as by-products. The products were first separated by liquid chromatography over the silica gel column. The low-molecular weight products including polydienes were eluted by hexane whereas inorganic products of the catalyst quenching and high-molecular weight polyolefins were retained. The product mixtures were in most cases difficult to separate without using *e.g.*, preparative GC chromatography, nevertheless, the products were identified by GC-MS chromatography. The yields of the 1 : 1 and 2 : 1 diene-to-BSD cycloadducts depended on the capability of the dienes to homooligomerize or polymerize. Among the dienes, butadiene is known to easily cyclotrimerize with the $(C_2H_5)_2AlCl/TiCl_4$ catalytic system to give a mixture of *cis,trans,trans*- and *trans,trans,trans*-1,5,9-cyclododecatrienes[13] (CDT). Indeed, a mixture of the 1 : 1 cycloadduct and the CDT isomers was obtained even at the 1 : 1 molar ratio of BSD and BUT. Their retention times on an SE-30 GC column were close to each other and thus the separation of the 1 : 1 adduct from the CDT isomers either by distillation or by liquid chromatography would be difficult. Therefore, a large excess of BUT (18.3 mmol) with respect to BSD (5.15 mmol) was applied and this resulted in obtaining a mixture of CDT isomers and the 2 : 1 adduct **1** (Scheme 1).



SCHEME 1

1

More volatile CDT isomers were removed by vacuum distillation at 100 °C and pure **1** was then distilled from a little amount of polymeric residue. The isolated yield 52% of **1** related to BSD indicated that some part of BSD was also involved in the polymerization. Compound **1** was identified as bis(2-trimethylsilylcyclohexa-1,4-dien-1-yl) by ^{1}H and ^{13}C NMR and mass spectroscopy. The NMR spectra were assigned using ^{1}H, ^{13}C, ^{1}H-COSY, ^{1}H-^{13}C HETCOR, and ^{1}H-^{13}C HETCOR optimized for the detection of small coupling constants (long range HETCOR). Carbon atoms are numbered as shown in formula **1** of Scheme 1 and protons are referred to the number of the carbon atom which they are attached to. Long range HETCOR proves that the trimethylsilyl group is coupled to the quatenary carbon atom resonating at 127.58 ppm (C-2). The olefinic proton showing a long-range coupling to the same carbon is then assigned to H-4, resonating at 5.717 ppm. The other olefinic proton, H-5, is coupled to the other quaternary carbon, denoted (C-1). H-5 is also long-range coupled to C-3, and H-4 is coupled to C-6. Normal HETCOR shows the short-range couplings. ^{1}H-COSY shows the existence of a $–CH_2–CH=CH–CH_2–$ spin system. This leads to a 1,4-cyclohexadiene structure. The missing substituent at C-1 requires the structure of a symmetric dimer, in agreement with the mass spectrum showing the molecular ion $M^{+\bullet}$ *m/z* 302. The dehydrogenation of **1** at 250 °C afforded 2,2′-bis(trimethylsilyl)biphenyl (**2**) in virtually quantitative yield (Scheme 2).



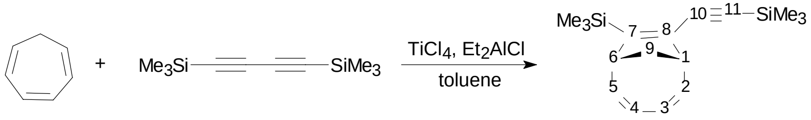
SCHEME 2

2

Analogous reactions of BSD with DMB (DMB : BSD = 17.0 : 5.15) afforded the crude product mixture which contained the hexane-soluble polydiene as a major product. The GC-MS analysis revealed the presence of 1 : 1 cycloadduct ($M^{+\bullet}$, *m/z* 276) in *ca* 80% amount, 5% of 2 : 1 cycloadduct ($M^{+\bullet}$, *m/z* 358) and the unreacted BSD 10%. The presence of BSD indicates that at least 12 mmoles of DMB out of 17 were involved in the polymerization. When a higher excess of DMB was used (BSD 2.6 mmol and DMB 17.0 mmol) all BSD was consumed, the 1 : 1 and 2 : 1 adducts were formed in comparable quantities, and a small amount of the DMB dimer ($M^{+\bullet}$, *m/z* 164) was also found. The reaction of BSD with CXD (BSD 5.15 mmol, CXD 16.0 mmol) produced mainly the polymer which was not retained in the column. The volatile products consisted mainly of a dimer of CXD ($M^{+\bullet}$, *m/z* 160) and minor amounts of the 1 : 1 and 2 : 1 adducts in approximately 1 : 2 ratio. Since no free BSD was detected it has to be assumed that it copolymerized with CXD. No attempts were, however, made to establish the polymer composition or its structure.

The reaction of BSD (5.15 mmol) with 1,3,5-cycloheptatriene (CHT, 9.6 mmol) affords a high yield of 1 : 1 cycloadduct **3** arising from the [6+2] addition (Scheme 3).

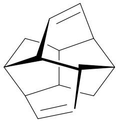
The structure of **3** follows from fully assigned ^{1}H and ^{13}C NMR spectra. Long-range HETCOR shows one TMS-group to be coupled to an sp^2-carbon atom (C-7, 146.84 ppm), the other TMS-group coupled to an acetylenic carbon (C-11, 95,77 ppm) and the upfield methylene proton to be coupled with both quaternary olefinic carbons. One methine proton shows a coupling with the acetylenic C-10 carbon atom and is therefore assigned to H-1. With this starting point and the results of the ^{1}H-COSY, the other protons could be assigned. The assignment of other carbon atoms is based on the ^{1}H-^{13}C HETCOR experiments. Minor volatile impurities are the pentacyclic dimers of CHT **4** and **5** which nearly quantitatively arise from the catalytic action of the $(C_2H_5)_2AlCl/TiCl_4$ system on cycloheptatriene[14,15]. The mechanism of their formation involves the initial [6+2] addition step followed by the [4+2] intramolecular cyclization[14].



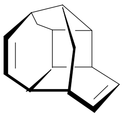
Scheme 3

3

At lower excess of CHT, a portion of BSD remains unreacted while a mixture of **3** with approximately 6% of **4** and **5** is obtained, as in the above optimized experiment. Their GC retention times on SE-30 column are very similar, and this precludes the easy separation of **3** from **4** and **5**. At higher excess of CHT, largely the dimers are obtained as the 2 : 1 cycloadduct of CHT and BSD is formed only reluctantly. Using 19.3 mmol of CHT and 5.5 mmol of BSD, the GC analysis afforded following yields: 2 : 1 adduct 6%, **3** 16%, and dimers of CHT 70%.



4



5

The cycloaddition reactions undoubtedly proceed in the coordination sphere of a low-valent titanium complex[3,4,16], as it has been outlined for the addition reactions of BTMSA. The present results, however, show that BSD is so weakly coordinated that the catalytic activity of the $(C_2H_5)_2AlCl/TiCl_4$ system in the polymerization of DMB and CXD, the cyclotrimerization of BUT or the dimerization of CHT are not significantly hindered. This is the main disadvantage of BSD compared to BTMSA whose apparently stronger complexation to the titanium species suppressed its polymerization and homooligomerization activities.

EXPERIMENTAL

Chemicals

1,4-Bis(trimethylsilyl)buta-1,3-diyne (BSD) was obtained by the reaction of perchlorobutadiene with trimethylsilyl chloride in the presence of a large excess of magnesium turnings according to described procedure[9]. Recrystallization was carried out from ethanol and finally from hexane. The purity was checked by GC-MS. 1,3-Butadiene and 1,3,5-cycloheptatriene (both Fluka) and toluene (Lachema, Brno) were distilled *in vacuo* and stored for several days as the solutions of dimeric titanocene[17]. They were then distributed into ampoules by vacuum distillation. $TiCl_4$ (International Enzymes) was refluxed with copper wire and then distilled *in vacuo* and diluted with toluene to give 0.1 M solution. $(C_2H_5)_2AlCl$ (Fluka) was purified from traces of $(C_2H_5)AlCl_2$ by heating with anhydrous sodium chloride to 180 °C. Then it was distilled *in vacuo* and diluted with toluene to give 1.0 M solution. Authentic compounds **4** and **5** (ref.[15] were used for their identification in the reaction products by gas chromatography.

Methods

^1H and ^{13}C NMR spectra (δ, ppm; *J*, Hz) of the products were measured on a Varian VXR-400 spectrometer (400 and 100 MHz, respectively) in $CDCl_3$ at 25 °C using the residual signal of the solvent as a reference. Infrared spectra (wavenumbers in cm^{-1}) of the liquid films were obtained on a UR-75 instrument (Zeiss, Jena). The GC analyses were performed on a CHROM 5 gas chromatograph (Laboratorni pristroje, Prague) using 10% SE-30 on a Chromaton N-AW-DMCS column. Analogous GC-MS analyses were carried out on a Hewlett–Packard gas chromatograph (5890 series II) equipped with a capillary column SPB-1 (length 30 m; Supelco) and a mass spectrometric detector (5971 A).

General Procedure for Cycloadditions of BSD

In a typical experiment, crystalline BSD (1.0 g, 5.4 mmol) was charged into an ampoule and was degassed on a vacuum line. The 1 M toluene solution of $(C_2H_5)_2AlCl$ (4 ml) was added from an attached ampoule. After BSD had dissolved, the solution was cooled by liquid nitrogen. Then, 0.1 M $TiCl_4$ in toluene (4 ml) was added from another ampoule. The reaction mixture was warmed to room temperature with shaking and then heated to 60 °C for 15 min to give a brown, homogeneous solution. Then, the solution was cooled by liquid nitrogen and the conjugated diene or CHT was distilled into the reaction mixture. The system of dosing ampoules was then sealed off and the reaction ampoule was heated to 60 °C for 8 h. After cooling to room temperature, the ampoule was opened and a brown, heterogeneous reaction mixture was poured onto a silica gel column (15 mm diameter, length 100 mm). An exothermic reaction occurred as the organometallic compounds were hydrolyzed by the water contained in the silica gel. The organic products were eluted from the column by hexane whereas inorganic products of hydrolysis remained in the column. The solvents were evaporated on a vacuum rotary evaporator and the crude product was analyzed by GC-MS or GC. The estimates of the product composition were obtained from integrated areas of GC peaks using an integrator and considering the number of C atoms in the molecule of the product components.

Bis(2-trimethylsilylcyclohexa-1,4-dien-1-yl) (**1**)

Butadiene (1.6 ml, 18.3 mmol) was applied in the above experiment. The crude product (1.4 g) contained according to GC analysis 77% of **1** and 21% of a mixture of *cis*,*trans*,*trans*- and *trans*,*trans*,*trans*-1,5,9-cyclododecatrienes and traces of unidentified compounds. The cyclododecatrienes were removed by vacuum distillation at 100 °C. The distillation at higher temperatures (100–140°C) afforded a nearly colourless **1** of 99% purity. Yield 0.8 g (52% related to BSD). The compound was identified on the basis of MS, ^{1}H and ^{13}C NMR spectra. IR spectrum (neat): 3 019 m, 2 948 s, 2 888 m, 2 866 m, 2 843 m, 2 803 m, 1 667 m, 1 592 m, 1 445 w, 1 420 s, 1 400 m, 1 246 vs, 1 168 vw, 1 090 m, 1 012 m, 908 m, 868 s, 835 vs, 755 s, 729 w, 685 m, 663 s, 609 w. Mass spectrum, *m/z* (%): 302 ($M^{+\bullet}$, 2); 211 (7); 197 (7); 195 (12); 160 (7); 159 (13); 155 (29); 154 (34); 135 (5); 74 (8); 73 (100); 59 (14); 45 (19). ^{1}H NMR spectrum ($CDCl_3$): 0.08 s, 9 H (TMS); 2.54 m, 1 H (H-6u); 2.71 m, 2 H (H-3); 2.83 m, 1 H (H-6d); 5.71 m, 1 H (H-5); 5.72 m, 1 H (H-4). ^{13}C NMR spectrum: –0.30 q, 3 C (TMS); 28.90 t (C-3); 32.37 t (C-6); 123.81 d (C-5); 128.69 d (C-4); 127.58 s (C-2); 147.39 s (C-1).

2,2′-Bis(trimethylsilyl)biphenyl (**2**)

Compound **1** (1.1 g) was degassed in an ampoule (200 ml) and this was sealed out. The ampoule was heated to 250 °C for 15 h and then was opened to air (*Attention: do not use flame as the ampoule contains hydrogen*). The yellowish liquid was distilled *in vacuo* to give colourless **2**. GC-MS analysis revealed the presence of **1** to be less than 0.5%. Yield 0.9 g (82%). IR spectrum (neat): 3 047 m, 2 944 s, 2 892 m, 1 920 w, 1 853 vw, 1 814 vw, 1 580 m, 1 449 m, 1 416 s, 1 306 vw, 1 247 vs, 1 119 s, 1 090 m, 1073 w, 1 042 w, 999 w, 843 sh, 833 vs, 770 sh, 754 s, 727 s, 686 m, 619 m, 557 w, 465 m. Mass spectrum, *m/z* (%): 298 ($M^{+\bullet}$, 6); 224 (12); 196 (19); 195 (100); 165 (17); 74 (7); 73 (81); 45 (16). ^{1}H NMR spectrum ($CDCl_3$): 0.04 s, 18 H (2 × $SiMe_3$); 7.187 m, 2 H; 7.355 m, 4 H; 7.609 m, 2 H. ^{13}C NMR spectrum: 0.35 q, 6 C (2 × $SiMe_3$); 126.39 d, 2 C; 127.69 d, 2 C; 129.89 d, 2 C; 134.29 d, 2 C; 138.83 s, 2 C (C-2, C-2’); 149.90 s, 2 C (C-1, C-1’). The NMR and mass spectra are in agreement with ref.[18].

7-Trimethylsilyl-8-trimethylsilylethynylbicyclo[4.2.1]nona-2,4-diene (**3**)

1,3,5-Cycloheptatriene (1 ml, 9.6 mmol) was applied in the general procedure described above. The isolated crude product (1.4 g) contained, according to GC analysis, **3** (91%), dimers of CHT **4** and **5** (6%) and traces of more volatile unidentified by-products (3%). The crude product was distilled under dynamic vacuum (*ca* 1 Pa) with the temperature rising up to 140 °C. The first 6 drops were separated. The main fraction (0.9 g) contained **3** 97% and **4** (2%) and **5** (1%). Yield of **3** was *ca* 60% related to BSD. This fraction was further distilled *in vacuo*, and the middle fraction (0.3 g) contained **3** in 99% purity. This was used for the structure identification by NMR spectroscopy. IR spectrum (neat): 3 013 m, 2 951 s, 2 930 sh, 2 893 m, 2 133 s, 1 532 w, 1 438 w, 1 403 m, 1 380 m, 1 313 m, 1 285 vw, 1 246 vs, 1 213 vw, 1 177 vw, 1 137 m, 1 073 w, 1 050 vw, 1 024 m, 1 004 w, 942 m, 896 w, 873 s, 859 sh, 837 vs, 755 s, 721 s, 698 m, 660 vw, 627 m, 613 m, 577 vw, 545 w, 524 w, 489 m, 461 vw, 430 w. Mass spectrum, *m/z* (%): 286 ($M^{+\bullet}$, 17); 271 (5); 213 (5); 212 (6); 199 (5); 198 (23); 197 (31); 184 (5); 183 (24); 181 (5); 179 (9); 155 (8); 145 (5); 121 (5); 116 (7); 107 (5); 97 (10); 93 (5); 92 (27); 91 (33); 83 (7); 79 (5); 74 (9); 73 (100); 59 (9); 45 (18); 43 (10). ^{1}H NMR spectrum ($CDCl_3$): 0.18 s, 9 H (TMS, C-11); 0.19 s, 9 H (TMS, C-7); 1.50 d, 1 H, J = 11.6 (H-9 endo); 2.08 m, 1 H (H-9 exo); 3.21 dd, 1 H, J = 7.5, 6.7 (H-6); 3.34 dd, 1 H, J = 7.6, 6.9 (H-1); 5.87 ddd, 1 H, J = 11.0, 7.4, 1.2 (H-4), 5.89 ddd, 1 H, J = 11.0, 7.4, 1.2 (H-3); 6.07 dddd, 1 H, J = 11.0, 7.5, 1.2, 1.1, 1.1 (H-5); 6.17 dddd, 1 H, J = 11.0, 7.6, 1.2, 1.2, 1.1 (H-2). ^{13}C NMR spectrum: –0.67 q, 3 C (TMS, C-11); –0.12 q, 3 C (TMS, C-7); 30.62 t (C-9), 48.32 d (C-6); 49.72 d (C-1); 95.77 s (C-11); 103.19 s (C-10); 124.49 d (C-4); 124.81 d (C-3); 125.32 s (C-8); 137.42 d (C-5); 137.64 d (C-2); 146.84 s (C-7).

This work was supported by the Grant Agency of the Academy of Sciences of the Czech Republic (Grant No. A440403).

REFERENCES

1. Vollhardt K. P. C.: Acc. Chem. Res. *10*, 1 (1977).
2. Schore N. E.: Chem. Rev. *88*, 1081 (1988).
3. Mach K., Antropiusova H., Turecek F., Hanus V., Sedmera P., Schraml J.: J. Organomet. Chem. *289*, 331 (1985).
4. Mach K., Antropiusova H., Petrusova L., Hanus V., Turecek F., Sedmera P.: Tetrahedron *40*, 3295 (1984).
5. Mach K., Antropiusova H., Sedmera P., Hanus V., Turecek F.: J. Chem. Soc., Chem. Commun. *1983*, 805.
6. Mach K., Antropiusova H., Hanus V., Sedmera P.: Collect. Czech. Chem. Commun. *54*, 3088 (1989).
7. Klein R., Sedmera P., Cejka J., Mach K.: J. Organomet. Chem. *436*, 143 (1992).
8. Klein R., Schmid G., Thewalt U., Sedmera P., Hanus V., Mach K.: J. Organomet. Chem. *466*, 125 (1994).
9. Ballard D. H., Gilman H.: J. Organomet. Chem. *15*, 321 (1968).
10. Kruerke U., Hubel W.: Chem. Ber. *94*, 2829 (1961).
11. Troyanov S.I., Varga V., Mach K.: Organometallics *12*, 2820 (1993).
12. Rosenthal U., Gorls H.: J. Organomet. Chem. *439*, C36 (1992).
13. Polacek J., Antropiusova H., Petrusova L., Mach K.: J. Mol. Catal. *70*, 9 (1991).
14. Mach K., Antropiusova H., Turecek F., Hanus V., Sedmera P.: Tetrahedron Lett. *21*, 4879 (1980).
15. Turecek F., Hanus V., Sedmera P., Antropiusova H., Mach K.: Collect. Czech. Chem. Commun. *46*, 1474 (1981).
16. Mach K., Turecek F., Antropiusova H., Hanus V.: Organometallics *5*, 1215 (1986).
17. Antropiusova H., Dosedlova A., Hanus V., Mach K.: Transition Met. Chem. (Weinheim, Germany) *6*, 90 (1981).
18. Gross U., Kaufmann D.: Chem. Ber. *120*, 991 (1987).