Generation and Interception of Isodicyclopentadiene Tautomers by Diene Transmissive Diels-Alder Reaction of a 1,5-Dihydropentalene with a Variety of Dienophiles

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The cycloaddition of *N*-methyl-1,2,4-triazoline-3,5-dione (MTAD), dimethyl acetylenedicarboxylate (DMAD), maleic anhydride (MA), and *p*-benzoquinone (BQ) with 6-methyl-4-phenyl-1,5-dihydropentalene (1) afforded the mono- and bis-adducts which depended on the dienophilic strength and reaction conditions (temperature, concentration). Thus, for the highly reactive dienophiles MTAD and DMAD, exclusively the bis-adducts (**2**, **3**) were isolated in high yields as products of diene transmissive Diels-Alder reactions; the corresponding mono-adducts (substituted isodicyclopentadienes) were not detected even as transients. The π-facial selectivity was high (>95% anti selectivity for **2** and **3**) for the second addition step, but it decreased to 75% when high substrate concentrations were used (formation of 25% of the syn product **3b**). In the case of the less reactive dienophiles MA or BQ, the corresponding intermediary mono-adducts could be detected by ^{1}H NMR spectroscopy and their conversion to the more stable isodicyclopentadiene tautomers (e.g. **4a** to **4b**) monitored directly in the reaction mixture. Both tautomers could be trapped intermolecularly for the MA case by addition of MTAD (**5**, **7**) or another equivalent of MA (**6**, **8**). The intramolecular cycloaddition of the isodicyclopentadiene tautomer derived from BQ and **1**, namely the mono-adduct **10b**, led to the cage compound **11**. The double cycloaddition of dienophiles to 1,5-dihydropentalenes provides an efficient and convenient methodology for the synthesis of complex polycyclic ring skeletons.

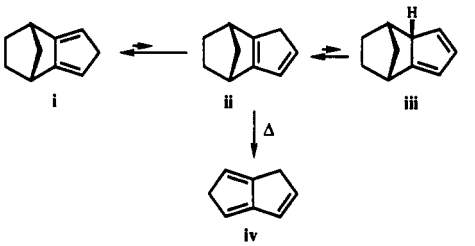
Introduction

The Diels-Alder reactivity of isodicyclopentadiene (**i**) and similar fused cyclopentadienes has been the subject of intensive investigation because of the exceptionally high facial selectivity exhibited during the course of the cycloaddition reaction with various dienophiles.[1-3] The starting material is available through the long-known dehydration route of dicyclopentenol (from dicyclopentadiene), developed by Alder et al.[4] and Katz et al.[5] As isodicyclopentadiene is formally a cyclopentadiene fused to a norbornane ring skeleton, it undergoes readily 1,5-hydrogen migration and exists in equilibrium with its thermodynamically less favored tautomers **ii** and **iii** (Scheme I). Recent work by Bartlett[6] and Paquette[7] showed that dienophiles with low reactivity are able to trap the minor isomers, which consequently must be *more* than 10^4 times as reactive than the dominating isomer **i**. Bartlett could even generate the pure isomer **iii** by deprotonation and reprotonation of **i**.[8] All experiments, therefore, have used **i** as starting material.

1,5-Dihydropentalene (**iv**) constitutes a suitable starting material for the controlled generation of derivatives of the dicyclopentadiene isomer **ii**. This has been shown in the synthesis of a bis(azoalkene) by using the parent 1,5-dihydropentalene (**iv**) as basis.[9] While the parent dihydropentalene **iv** was initially prepared by pyrolysis of isodicyclopentadiene **i** at ca. 575 °C under ethylene extrusion,[5] various substituted 1,5-dihydropentalenes are conveniently accessible from α,β-unsaturated ketones by a two-step procedure.[10] Such 1,5-dihydropentalenes are stable materials, which do not undergo hydrogen migration or dimerization reactions under ambient conditions. On the other hand, they are reactive dienes and even only moderately reactive dienophiles can be added; the course of the reaction, however, depends dramatically on the nature of the dienophile.

In this paper, we report a useful method for the independent generation of substituted isodicyclopentadiene tautomers by cycloaddition of a variety of dienophiles, e.g., *N*-methyl-1,2,4-triazoline-3,5-dione (MTAD), dimethyl acetylenedicarboxylate (DMAD), maleic anhydride (MA), and *p*-benzoquinone (BQ), to 6-methyl-4-phenyl-1,5-dihydropentalene (**1**), the latter readily available through the above described methodology.[10] Depending on the reactivity of the dienophile and the reaction conditions, the in situ generated substituted isodicyclopentadienes react further at their dienic moiety to add a second molecule of the dienophile. This diene-transmissive Diels-Alder re-

Scheme I



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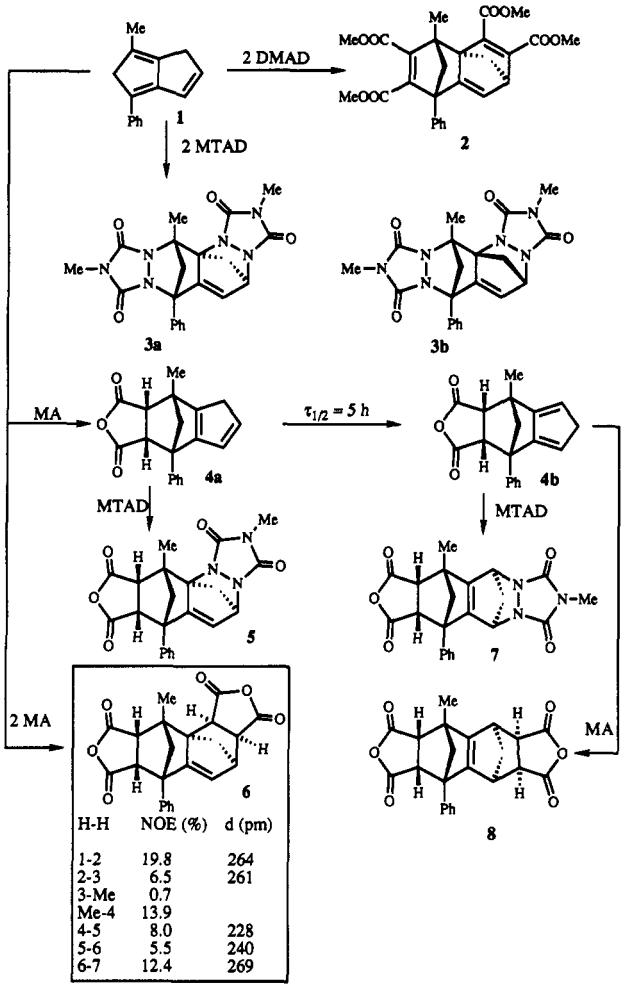
Scheme II



action with substituted 1,5-dihydropentalenes constitutes an effective and efficient route for the synthesis of complex, polycyclic ring skeletons.

Results and Discussion

The model 6-methyl-4-phenyl-1,5-dihydropentalene (**1**) was prepared by the literature procedure[10] in 68% yield. As highly reactive dienophiles, dimethyl acetylenedicarboxylate (DMAD) and *N*-methyl-1,2,4-triazoline-3,5-dione (MTAD) were employed and under all conditions the bis-adducts **2**, **3a**, and **3b** were formed as sole products; no mono-adducts could be detected by NMR spectroscopy. Even when an equimolar amount of dienophile was applied, only the bis-adducts were isolated besides unreacted triene **1**.

The stereochemistry of the MTAD adduct **3a** was determined by NOE measurements. Clearly, the two methylene bridges in the isosesquinorbornane ring system are trans to one another, which means that the second molecule of MTAD has approached the initially formed isodicyclopentadiene molecule anti with respect to the N–N bridge. This is analogous to the preferred direction of addition toward the isodicyclopentadiene isomer **ii** (anti with respect to the ethylene bridge).[7] The same π-facial selectivity has been observed in the MTAD cycloaddition with a substituted isoindane, where the relative configuration has been proven by means of crystal structure analysis.[11]

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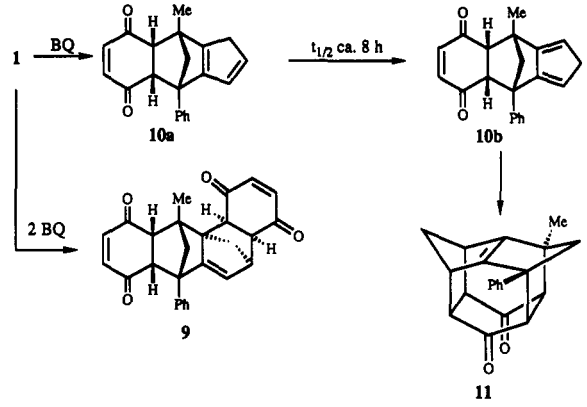
Scheme III



When **1** was allowed to react with a high concentration of MTAD at *room temperature* (ca. 2 M in $CHCl_3$), the bis-adduct **3a** and also its diastereomer **3b** were formed (ratio of 3:1) (Scheme II). Higher reaction temperatures could not be applied because of rapid decomposition of the Diels–Alder products. The syn stereochemistry of **3b** was determined by NOE measurements, which is clearly established by the mutual enhancements of the methylene bridge hydrogens. Under the above reaction conditions, MTAD or DMAd were reactive enough as dienophiles to intercept all of intermediary mono-adduct (type **ii**) directly after formation. When higher concentrations of both substrates were used and the reaction was carried out at room temperature, the π-facial selectivity decreased (see above). However, no cycloaddition products from the rearranged isodicyclopentadiene tautomers of type **i** could be detected.

When the less reactive dienophiles maleic anhydride (MA) and 1,4-benzoquinone (BQ) were used, a different product picture was observed that concerns single versus double cycloaddition. Thus, on the addition of 0.95 equiv of MA to **1** at 0 °C, after 5 min the mono-adduct **4a** could be registered as the sole product by NMR analysis of the crude product mixture. When another equivalent of a different dienophile was administered, e.g., MTAD, the mixed bis-adduct **5** was obtained. Two equiv of MA right from the beginning gave the bis-adduct **6**. NOE measurements showed that both methylene bridges possess an anti configuration (corresponding to the adducts **2**–**3**) and both anhydride moities an endo configuration. The important NOE enhancements are given in Scheme II with the corresponding internuclear distances (pm) from force field calculations.[12]

When a solution of the monoadduct **4a** was kept in $CDCl_3$ at room temperature, conversion of its isomer **4b** took place with a half-life of $\tau_{1/2}$ ca. 5 h. After completion of this 1,5-hydrogen shift, **4b** was treated with 1 equiv of MTAD or MA, which afforded the adducts **7** and **8**. Again NOE experiments uncovered their stereochemistry, in which the methylene bridges are anti to one another, completely analogous to the *directly* formed bis-adducts **5** or **6**. The cycloaddition of 2 equiv of 1,4-benzoquinone (BQ) with dihydropentalene **1** in methylene chloride afforded nearly quantitatively the bis-adduct **9** with the anti,endo,endo configuration. This adduct was formed to the extent of about 20–25% even when an equimolar amount of BQ and **1** was used.

More interesting is the second product **11**, which was obtained in about 30–35% yield after ca. 8–9 h. That this novel cage compound was produced by the sequence **10a**

(12) PC MODEL, Serena Software, Bloomington, IN.

→ **10b** → **11**, i.e., valence isomerization of the mono-adduct **10a** by 1,5-H sigmatropic shift to afford **10b** and subsequent intramolecular trapping (Scheme III), was established by means of ^{1}H NMR monitoring of the progress of the reaction course directly on the product mixture.

In summary, the advantage of the 1,5-dihydropentalene route to isodicyclopentadiene tautomers presented here is the fact that it serves as direct route to the thermodynamically unfavored isomers of the type **ii**. The latter are separated from the thermodynamically preferred type **i** by an appreciable activation energy, which permits trapping with the dienophiles employed herein.

Experimental Section

General Aspects. Thin-layer chromatography (TLC), Poligram SIL/G/UV 254 (Machery and Nagel); radial chromatography, Harrison Research Chromatotron on silica gel plates (2 mm). Combustion analyses were obtained in-house. Reagents and solvents were purchased from standard chemical suppliers and purified to match the reported physical and spectral data. Dihydropentalene **1** was prepared as previously reported.[10]

General Procedure for Double Cycloadditions. To a solution of **1** in CH_2Cl_2 at −78 °C was added a solution of 2.0 equiv of dienophile (DMAD, MTAD, MA, BQ) in CH_2Cl_2. After being stirred for 10 min at −78 °C, the solution was warmed to ca. 20 °C and stirred until completion of the reaction, the solvent rotary-evaporated (ca. 20 °C (20 Torr)), and the residue recrystallized or chromatographed on silica gel.

General Procedure for Single Cycloadditions. To a solution of 10 mmol of **5** in CH_2Cl_2 at −78 °C was added a solution of 0.98 equiv of dienophile (MA, BQ) in CH_2Cl_2. After being stirred for 10 min at −78 °C, the reaction mixture was allowed to warm to ca. 20 °C. When necessary, the reaction mixture was treated with another equivalent of the same or a different dienophile and worked up as described above.

Tetramethyl *anti*-1-Methyl-8-phenyltetracyclo-[6.2.1.1^{2,5}.0^{2,7}]dodeca-3,6,9-triene-3,4,9,10-tetracarboxylate (2). From 0.113 g (0.582 mmol) of **1** and 0.166 g (1.16 mmol) of DMAD in 35 mL of CH_2Cl_2 and stirring at ca. 20 °C for 10 h was obtained after chromatography (silica gel, 3:1 PE/EtOAc, R_f = 0.31) 0.261 g (94%) of **2** as a yellow wax: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.44 (s, 3 H), 1.94 (dd, 1 H, J = 1.9, 7.0 Hz), 2.37 (dd, 1 H, J = 1.9, 7.0 Hz), 2.39 (d, 1 H, J = 9.1 Hz), 2.87 (d, 1 H, J = 9.1 Hz), 3.50 (s, 3 H), 3.69 (s, 6 H), 3.76 (s, 3 H), 3.94 (m, 1 H), 6.49 (d, 1 H, J = 3.2 Hz), 7.18–7.31 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 13.9 (q), 51.5 (d), 52.0 (2q), 52.1 (2q), 52.4 (s), 60.4 (s), 64.6 (t), 74.9 (t), 80.3 (s), 127.2 (d), 127.4 (d), 128.4 (d), 128.9 (d), 136.6 (s), 145.7 (2s), 149.0 (s), 149.5 (s), 154.5 (s), 162.5 (s), 163.4 (s), 164.7 (s), 168.4 (s). Anal. Calcd for ($C_{27}H_{26}O_8$): C, 67.77; H, 5.48. Found: C, 67.59; H, 5.60.

***anti*-3,5,7,12,14,16-Hexaaza-1,5,14-trimethyl-11-phenylhexacyclo[9.5.1.1^{2,8}.0^{2,10}.0^{3,7}.0^{12,16}]octadec-9-ene-4,6,13,15-tetrone (3a).** From 1.11 g (5.71 mmol) of **1** and 1.30 g (11.50 mmol) of MTAD in 100 mL of CH_2Cl_2 and stirring at ca. 20 °C for 2 h was obtained after chromatography (silica gel, 1:1 PE/EtOAc, R_f = 0.27) 2.30 g (96%) of the bis-adduct as colorless needles, mp 160–161 °C dec: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.61 (dd, 1 H, J = 1.7, 9.2 Hz), 2.08 (s, 3 H), 2.33 (dd, 1 H, J = 1.7, 9.2 Hz), 2.74 (d, 1 H, J = 11.8 Hz), 2.91 (s, 3 H), 2.96 (s, 3 H), 3.60 (d, 1 H, J = 11.8 Hz), 5.06 (m, 1 H), 6.10 (d, 1 H, J = 2.3 Hz), 7.31 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 13.8 (q), 25.5 (q), 26.0 (q), 51.7 (t), 60.6 (t), 66.4 (d), 68.6 (s), 71.1 (s), 85.9 (s), 119.9 (d), 126.3 (d), 128.6 (d), 129.1 (d), 131.2 (s), 152.8 (s), 154.3 (s), 155.2 (s), 156.7 (s), 157.2 (s). Anal. Calcd for ($C_{21}H_{20}N_6O_4$): C, 59.99; H, 4.79; N, 19.99. Found: C, 60.12; H, 4.72; N, 20.12.

***syn*-3,5,7,12,14,16-Hexaaza-1,5,14-trimethyl-11-phenylhexacyclo[9.5.1.1^{2,8}.0^{2,10}.0^{3,7}.0^{12,16}]octadec-9-ene-4,6,13,15-tetrone (3b).** From 1.02 g (5.25 mmol) of **1** and 1.19 g (10.53 mmol) of MTAD in 5 mL of CH_2Cl_2 at ca. 20 °C and stirring for 2 h was obtained a mixture of the diastereomers **3a** and **3b** in a ratio of 3:1. After chromatography (silica gel, 1:1 PE/EtOAc, R_f = 0.31), 425 mg (19%) of the bis-adduct **3b** was isolated as colorless needles, mp 148–149 °C dec: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.83 (dd, 1 H, J = 1.7, 9.5 Hz), 2.04 (s, 3 H), 2.51 (dd, 1 H, J = 1.7, 9.4 Hz), 2.86 (s, 3 H), 2.88 (s, 3 H), 3.02 (d, 1 H, J = 12.8 Hz), 3.74 (d, 1 H, J = 12.8 Hz), 5.08 (m, 1 H), 6.06 (d, 1 H, J = 2.3 Hz), 7.37 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 13.9 (q), 25.5 (q), 26.0 (q), 52.6 (t), 57.9 (t), 65.1 (d), 66.1 (s), 72.8 (s), 84.9 (s), 117.9 (d), 128.3 (d), 128.7 (d), 129.6 (d), 130.8 (s), 152.2 (s), 154.3 (s), 154.9 (s), 156.2 (s), 157.0 (s). Anal. Calcd for $C_{21}H_{20}N_6O_4$: C, 59.99; H, 4.79; N, 19.99. Found: C, 59.81; H, 4.66; N, 20.41.

***endo*-1-Methyl-7-phenyl-4-oxatetracyclo[5.5.1.0^{2,6}.0^{8,12}]-trideca-8(12),9-diene-3,5-dione (4a).** To 77.1 mg (0.397 mmol) of **1** in 1 mL of CH_2Cl_2 was added 38.2 mg (0.390 mmol) of MA in 1 mL of CH_2Cl_2 and the solution stirred at ca. 20 °C for 10 min. The mono-adduct **4a** could only be observed *spectroscopically* directly on the crude product mixture: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.75 (s, 3 H), 2.15 (d, 1 H, J = 11.0 Hz), 2.25 (d, 1 H, J = 11.0 Hz), 2.82 (d, 1 H, J = 26.0 Hz), 3.20 (d, 1 H, J = 26.0 Hz), 3.56 (d, 1 H, J = 10.0 Hz), 4.05 (d, 1 H, J = 10.0 Hz), 6.45 (m, 2 H), 7.34–7.46 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 16.7 (q), 37.3 (t), 47.4 (s), 53.7 (d), 55.1 (d), 59.7 (s), 67.9 (t), 126.1 (d), 127.6 (d), 128.2 (d), 129.1 (d), 129.3 (s), 136.6 (d), 152.5 (s), 154.3 (s), 170.1 (s), 170.5 (s).

***anti,endo*-1,5-Dimethyl-11-phenyl-14-oxa-3,5,7-triazahexacyclo[9.5.1.1^{2,8}.0^{2,10}.0^{3,7}.0^{12,16}]octadec-9-ene-4,6,13,15-tetrone (5).** To 40.3 mg (0.208 mmol) of **1** in 1 mL of CH_2Cl_2 was added 20.2 mg (0.206 mmol) of MA in 1 mL of CH_2Cl_2 and the solution stirred at ca. 20 °C for 10 min. After the solution was cooled to −20 °C, 23.5 mg (0.208 mmol) of MTAD in 1 mL of CH_2Cl_2 was added and the solution stirred for 1 h at ca. 20 °C. Evaporation of the solvent and recrystallization from PE/EtOAc (5:2) gave 52.2 mg (62%) of bis-adduct **5** as yellow needles, mp 93–95 °C: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.70 (d, 1 H, J = 4.8 Hz), 1.87 (s, 3 H), 2.17 (d, 1 H, J = 4.8 Hz), 2.29 (d, 1 H, J = 11.7 Hz), 2.98 (s, 3 H), 3.69 (d, 1 H, J = 10.8 Hz), 3.77 (d, 1 H, J = 11.7 Hz), 4.08 (d, 1 H, J = 10.8 Hz), 5.10 (m, 1 H), 5.99 (d, 1 H, J = 2.5 Hz), 7.34–7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 15.5 (q), 25.8 (q), 50.0 (t), 54.1 (d), 55.4 (d), 55.6 (s), 59.2 (t), 62.5 (s), 65.5 (d), 88.1 (s), 121.1 (d), 126.8 (d), 128.1 (d), 128.9 (d), 135.2 (s), 155.1 (s), 15.6 (s), 158.2 (s), 168.4 (s), 169.7 (s). Anal. Calcd for $C_{22}H_{19}N_3O_5$: C, 65.18; H, 4.72; N, 10.36. Found: C, 65.01; H, 4.92; N, 10.62.

***anti,endo,endo*-5,14-Dioxa-1-methyl-11-phenylhexacyclo[9.5.1.1^{2,8}.0^{2,10}.0^{3,7}.0^{12,16}]octadec-9-ene-4,6,13,15-tetrone (6).** From 0.800 g (4.10 mmol) of **1** and 0.940 g (9.60 mmol) of MA in 40 mL of CH_2Cl_2 at ca. 20 °C for 7 h was obtained after recrystallization (*n*-pentane/10% $CHCl_3$) 1.49 g (92%) of bis-adduct **6** as colorless plates, mp 203–205 °C: ^{1}H NMR (acetone-d_6, 200 MHz) δ 1.76 (s, 3 H), 1.82 (d, 1 H, J = 11.0 Hz), 2.00 (d, 1 H, J = 11.0 Hz), 2.38 (d, 1 H, J = 11.3 Hz), 3.08 (d, 1 H, J = 11.3 Hz), 3.55 (m, 1 H), 3.95 (d, 1 H, J = 10.6 Hz), 4.05 (d, 1 H, J = 8.3 Hz), 4.12 (dd, 1 H, J = 5.3, 8.3 Hz), 4.48 (d, 1 H, J = 10.6 Hz), 5.88 (d, 1 H, J = 10.6 Hz), 7.25–7.55 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 15.7 (q), 46.9 (d), 47.5 (d), 48.0 (d), 49.8 (s), 52.8 (t), 54.3 (d), 55.6 (s), 55.8 (d), 58.4 (t), 69.6 (s), 123.9 (d), 126.6 (d), 127.2 (d), 128.5 (d), 137.4 (s), 158.0 (s), 170.4 (s), 171.4 (s), 171.8 (s), 173.3 (s). Anal. Calcd for $C_{23}H_{18}O_6$: C, 70.76; H, 4.65. Found: C, 70.51; H, 4.78.

***endo*-1-Methyl-7-phenyl-4-oxatetracyclo[5.5.1.0^{2,6}.0^{8,12}]-trideca-8,11-diene-3,5-dione (4b).** To 47.6 mg (0.245 mmol) of **1** in 1 mL of CH_2Cl_2 was added 23.8 mg (0.244 mmol) of MA in 1 mL of CH_2Cl_2 and the solution stirred at ca. 20 °C for 24 h. The mono-adduct **4b** could only be observed *spectroscopically* directly on the crude product mixture: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.70 (s, 3 H), 2.38 (d, 1 H, J = 11.0 Hz), 2.46 (d, 1 H, J = 11.0 Hz), 3.24 (m, 2 H), 3.53 (d, 1 H, J = 10.0 Hz), 3.93 (d, 1 H, J = 10.0 Hz), 5.89 (dd, 1 H, J = 1.2, 2.5 Hz), 5.99 (dd, 1 H, J = 1.2, 2.5 Hz), 7.30–7.49 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 15.9 (q), 46.0 (t), 49.5 (s), 54.8 (d), 55.5 (d), 57.7 (s), 61.3 (t), 120.6 (d), 121.6 (d), 127.2 (d), 127.6 (d), 128.6 (d), 137.8 (s), 151.0 (s), 151.5 (s), 170.5 (s), 171.2 (s).

***anti,endo*-1,6-Dimethyl-11-phenyl-14-oxa-4,6,8-triazahexacyclo[9.5.1.1^{3,9}.0^{2,10}.0^{4,8}.0^{12,16}]octadec-2(10)-ene-5,7,13,15-tetrone (7).** To 47.6 mg (0.245 mmol) of **1** in 1 mL of CH_2Cl_2 was added 23.8 mg (0.244 mmol) of MA in 1 mL of CH_2Cl_2 and the solution stirred at ca. 20 °C for 24 h. After the solution was cooled to ca. −20 °C, 27.7 mg (0.245 mmol) of MTAD in 1 mL of CH_2Cl_2 was added and the solution stirred at ca. 20 °C for 2 h. Crystallization from acetone yielded 78.2 mg (79%) of bis-adduct **7** as colorless

needles, mp 121–123 °C dec: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.64 (d, 1 H, J = 9.0 Hz), 1.68 (s, 3 H), 2.06 (d, 1 H, J = 9.0 Hz), 2.10 (d, 1 H, J = 9.3 Hz), 2.42 (d, 1 H, J = 9.3 Hz), 2.87 (s, 3 H), 3.64 (d, 1 H, J = 9.1 Hz), 3.89 (d, 1 H, J = 9.1 Hz), 5.10 (s, 1 H), 5.19 (s, 1 H), 7.36–7.45 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.9 (q), 25.5 (q), 53.6 (t), 54.2 (d), 54.3 (s), 55.7 (d), 61.3 (s), 63.0 (d), 64.3 (d), 68.4 (t), 126.9 (d), 128.2 (d), 128.7 (d), 135.4 (s), 151.9 (s), 152.0 (s), 159.0 (s), 159.9 (s), 170.9 (s), 171.2 (s). Anal. Calcd for $C_{22}H_{19}N_3O_5$: C, 65.18; H, 4.72; N, 10.36. Found: C, 64.86; H, 5.00; N, 10.41.

***anti,endo,endo*-1-Methyl-11-phenyl-6,14-dioxahexacyclo[9.5.1.1^{3,9}.0^{2,10}.0^{4,8}.0^{12,16}]octadec-2(10)-ene-5,7,13,15-tetrone (8).** To 52.0 mg (0.267 mmol) of 1 in 10 mL of CH_2Cl_2 was added 26.0 mg (0.265 mmol) of MA in 5 mL of CH_2Cl_2 and stirred at ca. 20 °C for 24 h. After the solution was cooled to −20 °C, 26.2 mg (0.267 mmol) of MA in 5 mL of CH_2Cl_2 was added and the solution stirred at ca. 20 °C for 2 h. Crystallization from ethanol yielded 83 mg (79%) bis-adduct 8 as yellow needles, mp 176–177 °C dec: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.52 (s, 3 H), 1.58–2.05 (complex m, consisting of 3 AB-systems, 6 H), 3.43–3.72 (m, 4 H), 7.33–7.45 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 15.1 (q), 45.7 (d), 46.9 (d), 48.0 (d), 48.5 (d), 54.5 (s), 54.8 (d), 55.8 (d), 59.0 (t), 62.3 (s), 67.2 (t), 127.8 (d), 128.6 (d), 128.8 (d), 136.4 (s), 155.2 (s), 155.8 (s), 170.0 (s), 170.4 (s), 170.6 (s), 171.5 (s). Anal. Calcd for $C_{23}H_{18}O_6$: C, 70.76; H, 4.65. Found: C, 71.02; H, 4.59.

***anti,endo,endo*-1-Methyl-12-phenylhexacyclo[10.6.1.1^{2,9}.0^{2,11}.0^{3,8}.0^{13,18}]eicos-10-ene-4,7,14,17-tetrone (9).** From 200 mg (1.03 mmol) of 1 and 230 mg (2.12 mmol) of BQ in 35 mL of EtOH and stirring at ca. 20 °C for 3 d was obtained, after recrystallization from MeOH/EtOH (5:1), 310 mg (75%) 9 as yellow plates, mp 184–186 °C: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.29 (dd, 1 H, J = 1.3, 8.9 Hz), 1.48 (dd, 1 H, J = 1.1, 8.9 Hz), 1.84 (d, 1 H, J = 11.1 Hz), 1.85 (s, 3 H), 2.08 (d, 1 H, J = 11.1 Hz), 3.31 (m, 2 H), 3.53 (m, 2 H), 4.21 (d, 1 H, J = 11.4 Hz), 5.77 (d, 1 H, J = 2.5 Hz), 6.68 (2 AB-systems, 4 H), 7.19–7.52 (m, 5 H); ^{13}C NMR acetone-d_6, 50 MHz) δ 16.5 (q), 49.5 (d), 50.8 (d), 52.6 (d), 52.9 (s), 54.2 (t), 55.8 (d), 56.6 (d), 57.2 (s), 58.9 (t), 73.7 (s), 125.5 (d), 127.0 (d), 127.6 (d), 128.8 (d), 140.6 (s), 142.6 (d), 142.8 (d), 143.0 (d), 143.5 (d), 158.6 (s), 197.4 (s), 199.2 (s), 199.8 (s), 202.1 (s). Anal. Calcd for $C_{27}H_{22}O_4$: C, 79.01; H, 5.40. Found: C, 79.12; H, 5.37.

1-Methyl-8-phenylhexacyclo[6.5.1.0^{2,7}.0^{4,12}.0^{5,10}.0^{9,13}]tetradec-9(13)-ene-3,6-dione (11). From 200 mg (1.03 mmol) of 1 and 113 mg (1.05 mmol) of BQ in 35 mL of EtOH after stirring at ca. 20 °C for 1 d was obtained after radial chromatography, besides 45.0 mg (21%) of 9, 87.0 mg (28%) of 11 (silica gel, 5:1 CH_2Cl_2/EtOAc, R_f = 0.45) as colorless needles: mp 106–108 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.42 (s, 3 H), 1.48 (dd, 1 H, J = 1.0, 10.2 Hz), 1.78 (d, 1 H, J = 10.2 Hz), 1.96 (ddd, 1 H, J = 1.3, 1.4, 10.2 Hz), 2.12 (d, 1 H, J = 10.2 Hz), 2.70 (dd, 1 H, J = 2.9, 8.1 Hz), 2.77 (m, 2 H), 3.21 (dd, 1 H, J = 2.6, 8.1 Hz), 3.51 (m, 2 H), 7.19–7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 15.1 (q), 42.5 (t), 51.7 (d), 52.5 (d), 56.0 (t), 56.8 (d), 57.2 (d), 60.2 (s), 62.9 (d), 65.3 (d), 68.4 (s), 127.3 (d), 128.7 (d), 138.8 (s), 148.3 (s), 155.4 (s), 158.1 (s), 210.3 (s), 210.5 (s). Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 5.99. Found: C, 83.68; H, 6.04.

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$(Me_3Si)_3SiH$: An Efficient Hydrosilylating Agent of Alkenes and Alkynes

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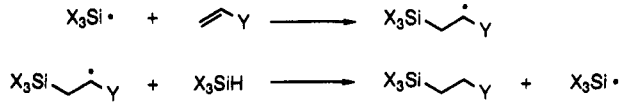
Tris(trimethylsilyl)silane adds across the double bond of a variety of mono-, di-, and trisubstituted olefins under free-radical conditions in good yields. The reaction, which proceeds via a free-radical chain mechanism, is highly regioselective (anti-Markovnikov). Addition to prochiral olefins bearing an ester group is highly stereoselective. The factors that control the stereochemistry have been discussed in terms of preferred conformations of the intermediate carbon-centered radicals and are thought to be of steric origin.

Introduction

Hydrosilylation of carbon–carbon multiple bonds has been studied extensively for the last half century.[2] The reaction is used for the production of organosilicon compounds on both industrial and laboratory scales and is an important method of forming silicon–carbon bonds. In the early years, the reactions were performed under free-radical conditions;[3-5] i.e., ultraviolet light or organic peroxides were widely used. The choice of substrates, however, was limited to silanes such as Cl_3SiH and $MeCl_2SiH$ and to C,C multiple bonds mostly with alkyl substituents. For example, oligomerization was a serious problem when olefins such as methyl acrylate were used.[4] With the discovery that transition metals and their complexes catalyze hydrosilylation, the photo- and peroxide-initiated reactions have been largely superseded.[2,6] Platinum catalysts, especially chloroplatinic acid, have become the most commonly used while other transition-metal catalysts of nickel, palladium, cobalt, rhodium, iridium, iron, ruthenium, and osmium have also been developed.[2] Some of these processes are very efficient irrespective of the nature of the silane and can be used for the simple preparation of a desired product or for asymmetric hydrosilylation. Recently, hydrosilylation catalyzed by metal colloids has also been reported.[7]

Scheme I



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